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ASD-TR-61-260
Part I, Vols. 1 and 2

May 1962

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The following addition is made to ASD Technical Report 61-260, Part I, Volumes 1 and 2 entitled "Thermodynamics of Certain Refractory Compounds":

Cover Pages

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Air Force Systems Command
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ASD-TR-61-260
PART I, VOL. 1

THERMODYNAMICS OF CERTAIN REFRACTORY COMPOUNDS

VOL. 1. LITERATURE SEARCH, COMPUTATIONS, AND PRELIMINARY STUDIES

TECHNICAL DOCUMENTARY REPORT No. ASD-TR-61-260
PT. I, VOLUME 1

MAY 1962

DIRECTORATE OF MATERIALS AND PROCESSES
AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Project Nos. 7350 & 7381, Task Nos. 73500 & 73812

(Prepared under Contract AF 33(616)-7327
by the Research and Advanced Development Division, Avco Corporation, Wilmington, Massachusetts; S. L. Bender, R. E. Dreikorn, T. H. Einwohner, R. C. Feber, R. E. Gannon, P. L. Hanst, M. E. Ihnat, J. P. Phaneuf, H. L. Schick, and C. H. Ward, authors.)

FOREWORD

This report was prepared by the Avco Research and Advanced Development Division under USAF Contract No. AF33(616)-7327. This contract was initiated under Project No. 7350, "Ceramic and Cermet Materials", Task No. 73500, "Ceramic and Cermet Materials Development"; and Project No. 7381, "Materials Application", Task No. 73812, "Data Collection and Correlation". The work was administered under the direction of the Directorate of Materials and Processes Deputy for Technology, Aeronautical Systems Division, with Mr. P. W. Dimiduk acting as project engineer.

This report covers work conducted from 1 May 1960 to 30 April 1961.

Assistance from a number of sources has given vital support to the work on this project. The authors wish to acknowledge contributions from Prof. W. Klemperer in giving advice on spectroscopic experiments, Dr. D. R. Stull of the Dow Chemical Co. for many valuable discussions, the loan of microfilms, etc., Mr. T. R. Munson for providing the program for the machine computations on diatomic molecules, Dr. G. T. Furukawa for counsel on methods of smoothing C_p^o data, the staff of the Avco RAD Mathematics Section in programming and computing machine assistance, Dr. Joan B. Berkowitz-Mattuck and Mr. S. N. Goldstein at the A. D. Little Company in providing translations of Russian articles, Dr. S. Ruby for interest in the work and supervisory assistance, Mr. T. Licht in making chemical analyses, Mr. P. F. Jahn in sample preparation, and Mr. R. E. Walters and Mrs. Ann Wise in the literature search. Other contributors at Avco RAD have been Messrs. J. K. Hill and P. Demenkow (assistance in X-ray diffraction studies), J. Achramowicz (sample preparation), V. H. Early (spectroscopic studies), E. J. Kay and D. V. LaRosa (coding and other assistance in the work with IBM cards and computations), D. A. Dreselly (manuscript preparation), L. Fitzpatrick (chemical analyses), and W. S. Bennett (glassblowing). Reprints, reports, and other sources of data were contributed by Mr. P. W. Dimiduk (ASD), Dr. K. K. Kelley (U. S. Bureau of Mines), Dr. G. M. Rosenblatt (Univ. of California), Dr. G. R. Somayajulu (Univ. of California), Dr. D. L. Hildenbrand (Aeronutronics), Dr. R. H. Crist (Union Carbide Corp.), Dr. J. L. Margrave (Univ. of Wisconsin), and Dr. C. W. Beckett and others at the National Bureau of Standards (Heat Division).

ABSTRACT

Theoretical and experimental studies were undertaken of the thermodynamics of certain refractory compounds from 298.15° to 6000°K. The list of compounds included the oxides, borides, carbides, and nitrides of the metals in groups IVB, VB, VIB, and VIIB of the periodic chart in addition to those of silicon, scandium, beryllium, magnesium, calcium, strontium, and osmium.

Tables of ideal gas thermodynamic functions of all the above elements were either prepared or brought up to date. Reviews and critical analyses of the available data were completed on the oxide systems of Be, Ca, Cr, Mg, Mo, Sr, Ti, and W, the borides of Ti, and the monocarbide of Ti. Sixty-one tables of thermodynamic functions, in various degrees of completion, were prepared on the important chemical species of the above systems.

A comprehensive review of the literature was made for the existing theoretical background needed in the interpretation of high-temperature C_p^o data and for the improvement of methods of estimating missing data.

In the experimental studies, careful checks were made of the purity of all samples. A Bunsen ice calorimeter apparatus was developed for specific heat measurements up to 1500°C. An apparatus employing the pulse method of specific heat measurements was used to make determinations in the temperature range from 1500° to 2500°C on borides of Mo, Ti, W, and Zr, on carbides of Nb, Ta, Ti, and Zr, and on a nitride of Ti. Spectroscopic studies were carried out on the Si-C, Mo-C, W-O, and the B-O system vapor species to determine their molecular structures and spectroscopic constants.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

Jules I. Wittebort

J. I. Wittebort
Chief, Thermophysics Branch
Physics Laboratory
Directorate of Materials and Processes

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I. INTRODUCTION

Contract AF33(616)-7327 has for its purpose the determination of the thermodynamic functions of a limited number of highly refractory compounds up to 6000°K. The scope of the contract encompasses the oxides, carbides, nitrides, and borides of elements in groups IIA, IVB, VB, VIB, VIIB, plus scandium, osmium, and silicon. This is summarized in figure 1 wherein the elements in the solid boxes are to be combined with those in the broken box to form the subject compounds. The metals Ir, Pt, and Rh were added to the list at the request of the project engineer.

The state of knowledge on these highly refractory compounds is such that much preliminary work was necessary to search for and to adapt required basic material property data before reliable computations could be made. Moreover, much of the existing data were inadequate, inaccurate, and in many cases even contradictory. Thus, only a limited number of the compounds could be completely characterized thermodynamically without a program of experimental measurements to provide additional basic data and to verify the existing data that are uncertain. Accordingly, the scientific effort on this project was distributed among three major phases as follows:

Phase I -- Review of the literature and compilation of all available data.

Phase II -- Calculation and tabulation of thermodynamic properties from available data.

Phase III -- Experimental studies to provide missing data, to prove the adequacy of computational techniques, and to verify any assumptions made throughout the program.

The list of basic data sought in Phase I includes not only those directly useful in the computations of Phase II, but also some that may find use in later applications of the thermodynamic functions. The list is as follows:

1. Phase diagrams
2. Heat capacity versus temperature
3. Enthalpy versus temperature
4. Entropy versus temperature
5. Heats of phase transformations
6. Heats of formation or reaction
7. Thermal expansion coefficients and compressibilities
8. Melting and triple points
9. Free energies of formation
10. Vapor pressures
11. Composition of gaseous species in vapor
12. Spectroscopic constants

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IIA	IIIB	IVB	VB	VIB	VIIB		IB	IIB	IIIA	IVA	VA	VIA	VIIA
													1 H
4 Be									5 B	6 C	7 N	8 O	9 F
12 Mg									13 Al	14 Si	15 P	16 S	17 Cl
20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn		29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br
38 Sr		40 Zr	41 Nb	42 Mo	43 Tc		47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I
		72 Hf	73 Ta	74 W	75 Re	76 Os	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At

Figure 1 AREAS OF PERIODIC CHART INCLUDING ELEMENTS WHOSE COMPOUNDS ARE THE SUBJECT OF THE PROJECT

13. Ionization or appearance potentials
14. Emf's of electrolytic cells
15. Heats of solution or dilution
16. Other thermodynamic functions.

The experimental studies of Phase III can be grouped into the following three categories:

a. Preparation of compounds and specimens. This includes analyses to verify purity and crystal structure, or the existence of special conditions such as extent of solid solution, etc.

b. Heat capacity and total heat content determinations with a pulse-method apparatus and a Bunsen ice calorimeter.

c. Spectroscopic studies of vapor species.

II. REVIEW OF THE LITERATURE AND COMPILATION OF AVAILABLE DATA

A. SCOPE OF THE LITERATURE SEARCH

The literature search has been very comprehensive, the intention being to cover all the literature of at least the last ten years. The following is a list of the literature sources searched:

1. Nat. Bur. Stds. Circular 500, Selected Values of Chemical Thermodynamic Properties (1952-1956).

2. Kubaschewski, O. and E. Evans, Metallurgical Thermochemistry, Pergamon Press, N. Y. (1958).

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21. Goldsmith, A., T. Waterman, and H.J. Hirschhorn, Thermophysical Properties of Solid Materials, WADC TR-58-476;

AD-207905 (January 1959),
Vol. 1. Elements, AD-247193 (August 1960),
Vol. 2. Alloys, WADC-58-476 (November 1960).

22. Goldsmith, A. et al, Additional volumes to supplement 21 above obtained from ASD and Armour Research Foundation.

23. Johnson, V. J., A Compendium of the Properties of Materials At Low Temperatures, Phase I, NBS, Boulder, Colorado (December 1959); WADD TR-60-56, Pts. I, II, and III.

24. Ann. Revs. Phys. Chem. (1950 - 1959).

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Ind. Eng. Chem. 50, 561 (1958)
Ind. Eng. Chem. 51, 472 (1959)
Ind. Eng. Chem. 52, 451 (1960)
Ind. Eng. Chem. 49, 583 (1957)
Ind. Eng. Chem. 48, 676 (1956)
Ind. Eng. Chem. 47, 664 (1955)

Ind. Eng. Chem. 46, 947 (1954)
Ind. Eng. Chem. 45, 963 (1953).

26. Sinke, G. C. et al, Thermodynamic Properties of Combustion Products, WADC and ARPA, Rept. AR-214-587, Dow Chem. (1 April 1959).

27. Beckett, C. W. et al, Preliminary Report on the Thermodynamic Properties of Lithium, Beryllium, Magnesium, Aluminum, and Their Compounds with Oxygen, Hydrogen, Fluorine, and Chlorine, Nat. Bur. Stds. (U. S.) Rept. 6297 (1 June 1959); Rept. 6484 (1 July 1959).

28. Beckett, C. W., et al, Preliminary Report on the Thermodynamic Properties of Selected Light-Element Compounds, Nat. Bur. Stds. (U. S.) Rept. 6645 (Supplement to Repts. 6297 and 6484), (1 January 1960, amended 1 April 1960). Also Rept. 6928 (Supplement to NBS Repts. 6297, 6484, and 6645), (1 July 1960).

29. Chem. Abstracts (1950-1961).

30. Nuclear Sci. Abstracts (1950-1961).

31. Eng. Index (1953-1958).

32. Phys. Abstracts (1950-1961).

33. Ceram. Abstracts (Recent Years).

34. Dissertation Abstracts (Recent Years).

35. IUPAC Bibliography (April 1960-1961).

36. Battelle Tech. Rev.

37. Monthly Index of Russian Accessions (Library of Congress), (1960).

The scope of the entire primary literature uncovered is best indicated by the list of references in the reference code file in section VII-B.

B. ACCUMULATED FILES

Four files have been accumulated as products of the literature search. The primary ASM card file contains all the information obtained and handwritten by the searchers and abstractors. All references were coded and punched into IBM cards for the second file. An author index file could have been made from duplicate IBM cards of the "L" type (described in section C). However, it was found more convenient to use printouts from the IBM cards (one for each abstractor) in place of the author index, whose purpose has been to expedite the elimination of duplicate references at the source and avoid needless repetition of effort. The IBM card file was intended to store all the information in a form that could be handled by sorting, collating, and computing machines. The fourth file is a subject index made up from the IBM card file.

C. DATA CODING AND IBM CARD FILE SYSTEM

1. Introduction

a. General Remarks

In the work on Phase I of this project, it has been necessary to store in readily accessible form large amounts of bibliographic information and numerical data on thermodynamic properties of certain chemical elements and compounds. In Phase II, it has been necessary to calculate thermodynamic properties by routine and often repeated procedures. The problems of information storage, retrieval, and modification, and calculation of related thermodynamic properties were expedited and simplified by the use of electronic calculators and sorting equipment available at Avco RAD. For this, a system for handling both bibliographic information and numerical data had to be developed.

The system was designed to treat one phase of the problem, that of storing the data in relatively accessible form when coded on standard IBM cards in a fixed format. By means of the IBM Sorter, information of any category could be easily culled out of the master file.

The following paragraphs describe the part of this system which was used extensively in the literature search and bibliographic work.

b. Mnemonic Symbols

Limited storage space, the unwieldliness of large files, and minimization of machine running time require symbols of minimum number of characters to describe categories of information, units, values, etc. On the other hand, this minimum length symbol might not easily be remembered and coding time would be lost in continual reference to a glossary and codes. A compromise has been reached in allowing the symbol to correspond as much as possible to the commonly accepted abbreviation. When shorter codes were required, the attempt was to make them correspond to the sound of the quantity being coded.

c. Structure of IBM Cards

For purposes of reference, the IBM card is divided into rows and columns. Columns are numbered consecutively 1 to 80 from left to right. Rows are numbered from top to bottom 12, 11, zero and 1 to 9. To record information in the card, a given character (i.e., number, letter, or special symbol such as *) is punched as a characteristic hole or series of holes, all in the same column. Any character can be punched into any column, but two or more characters cannot occupy the same column. The character can be simultaneously printed at the head of the column it occupies, allowing ready reading of information on the card. A number is represented by a single hole (or punch) in the given column. Thus, for example, the number 9 in column 73 would be represented by a punch in column 73 row 9. A letter is represented by two characteristic holes in the same column and a special character by three.

For more compact storage of information, one allows a punch in the 12, 11, or zero row of a column where numeric information is stored. Sometimes row 12 is called + and row 11 -. This is called an overpunch (O/p).

d. Fixed Field Format

Since a character occupies a column, a multicharacter symbol occupies a series of contiguous columns called a field. For ease in sorting, it is convenient to have all symbols of the same general type occupy the same columns on different cards. Thus, for example, suppose one denotes molar heat capacity at constant pressure by the symbol CP (all letters must be capitals and no subscripts or superscripts are allowed). The convention is made that, for a given series of cards, each card with a symbol for a thermodynamic property will have the property in columns 2-5. Then to distinguish cards with C_p data from those of other thermodynamic properties, sorts for C in column 2, P in column 3, and blanks in 4 and 5 are made. The cards selected in this way will have the desired information.

2. <u>Types of Cards</u>

In general, widely different types of information to be handled and sorted will result in different types of formats. For compatibility with other machines, which will eventually handle and use the data, the format of the rest of the card is denoted in column 1. The various types of cards are as follows:

Column 1	Meaning
D	Definition Card
L	Library Card
C	Comment Card
Other	Type A Card.

In all these cards, column 1 describes the type of card, 2 to 72 describe the information, and 73 to 80 are reserved for card identification.

3. Card Identification Format

To have absolute, sequential numbering of cards and reference to the person who took the abstract and the approximate date, the following format was used in columns 73 to 80 of cards of all types.

Column	Character	Meaning
73	α	One character symbol for month A = May 1960, B = June 1960, etc.
74	$\overset{o}{\nu}$	Abstractor. O/p indicates finder card
75 to 79	ν	Serial number
80	α'	Not used.

The explanation of character symbols is as follows:

- μ Numeric character
- $\overset{o}{\nu}$ Overpunched (O/p) numeric character
- α Alphabetic character
- α' Alphabetic or numeric character
- σ Special character
- b Blank.

4. Library Cards

It was supposed that several pieces of data would often be taken from the same reference. Each piece of data needs to be punched on a card which will also have coded the reference by journal, volume, page, and year. It would also be convenient to give further information about a given reference. For example, one might want to know the names of the authors or a reference to an abstract, if any. This information was recorded on the library cards, whose format is summarized below.

a. The symbols used in library card coding were as follows:

Column	Character	Meaning
1	L	Identifies library card.
2-11	10 *a*	Last name of first author. (The "10" means that the 10 columns (2-11) contain letters (alphabetic symbols).
12	, or *a*	A comma is the usual character, it is used to separate last name from the first initial. For last names of eleven or more letters however, the comma is replaced by the eleventh letter.
13	*a*	First initial of author's name. If the last name is eleven letters long however, this column is blank. If last name is twelve or more letters long, the twelfth letter of the author's name occupies this column.
14-22	9 *a*	Second author's name.
23	, or *a*	Follow the procedure indicated for column 12, unless last name contains ten or more letters, in which case comma is replaced by the tenth letter.

Column	Character	Meaning
24	α	First initial of second author's name. However if the last name is ten letters long, this column is blank. If last name is eleven or more letters long, the eleventh letter occupies this column.
25-29	5α	Five-letter symbol for the original reference. Column 25 must be α. Occasionally, numerical information is put in columns 27, 28, and 29. For example, a report with a designation AD-101-773 would have the AD-101 located in columns 25-29, while the 773 would be in columns 30-32.
30-32 (usual case)	3ν (see exceptions below)	Volume number of original reference. Several variations are possible for 30-32, 33, and 34-39.
30 (alternative 30-1)	R	Report number will be given in the following columns (31-39), using a fixed-field format (31, 32), (33, 34), (35, 36), (37, 38, 39). Dashes will be assumed but not written between columns 32 and 33, etc.
30 (alternative 30-2)	F	Report number will follow in (31-39), using a free field. Report numbers are given with no regard for field. Any combination of numbers and dashes can be used, but the dashes must be written explicity.
30 (alternative 30-3)	P	Paper number will follow, using same type of fixed field as for alternative 30-1 above.
32 (alternative 32-1)	*	Asterisk means no volume number is given.
32 (alternative 32-2)	+	Plus means volume number is the same as the year.

Column	Character	Meaning
33 (usual)	.	Comma is the usual symbol used to indicate that the page number of the original reference follows in columns 34-38.
33 (alternative 33-1)	or *	Means an abstract number follows in columns 34-38, rather than a page number.
33 (alternative 33-2)	or /	Means next two columns (34 and 35) contain issue number, while column 36 <u>must</u> contain another virgule, and page numbers are in columns 37-39.
33 (alternative 33-3)	or S	Means a supplement number will follow in column 34. Page numbers will be placed in columns (35-38).
33 (alternative 33-4)	or P	Means a part number of a report follows in column 34.
34-38 (usual case)	5 ν	Page number or abstract number of original reference. The smallest number is placed in column 38. This system is used if comma, or asterisk, is located in column 33.
39 (usual case)	a'	A letter or a number is used with the preceding page number to locate the column or row on the page where the reference is found. If this information is not available, this column is blank.
34-39 (alternative)		
Alternatives are available as described by 30-1, 30-2, 30-3, 32-1, 32-2, 33-1, 33-2, and 33-3.		
40	(or *	Beginning parenthesis means that original reference was consulted; asterisk means that data were taken from a source other than the original reference.

Column	Character	Meaning
41-42	$\overset{\circ}{\nu}\ \overset{\circ}{\nu}$	Last two figures of the year. A minus (-) overpunch in column 41 means nineteenth century. In column 42 a plus (+) overpunch means in Russian; a minus (-) overpunch means in German.
43-44	2 a	Symbol for abstracting journal. If the symbol has four characters, the last two characters are coded in columns 57-58.
45-46	2 ν	Volume number of abstract.
47	, or *	Comma denotes page number to follow; asterisk denotes abstract number to follow.
48-53	5 $\nu a'$	Page, column, or abstract number.
54	(or *	Same as column 40. Usually, the beginning parenthesis will be used here.
55-56	2 ν	Last two figures of the year of abstract publication.
57-58	2 a	Last two symbols for the abstracting journal.
59	a'	Character to denote availability of original reference (see paragraph b of this section).
60-69	10 a	Third author's last name.
70	,	Follow procedure for column 12.
71	a	First initial of third author's name (see procedure for column 13).
72	E or M	If more than 3 authors, use "E" (<u>et</u> <u>al</u>). If any of the author's names could not be completely coded; i. e., if any first initials are missing, use "M".

Column	Character	Meaning
73	a	A letter to designate month in which original ASM card was taken. Thus, May (1960) = "A"; June (1960) = "B" . . .
74-79	6ν	Serial number for original ASM card.
80	ν	This column is not used with "L" cards. However, "T" cards may have numbers starting with 1 in column 80. These indicate the order in which "T" cards should follow "L" cards in a bibliography.

b. A glossary of availability characters for column 59 of library cards follows:

Character	Meaning
L	Avco RAD Research Library.
E	Avco-Everett Technical Library.
M	MIT Library.
H	Harvard Libraries.
G	AFCRL* Library.
C	Avco Crosley.
N	Other nearby libraries (Boston area).
¢	Original on order.
ν	Abstractor with number.
P	Personnel at Avco RAD.
Z	Abstract not available at Avco RAD.
X	Original practically unavailable.

*Now, the Air Force Cambridge Research Laboratories, Bedford, Massachusetts; formerly AFCRC (the Air Force Cambridge Research Center).

5. Title Cards

Since title cards have a relatively free field, they were quite simple to prepare. The coding scheme has been as follows:

Column	Character	Meaning
1	T	Title card.
2	b	Must be blank.
3-72	70 a'	Case(1) (Author elaboration card). If an "E" or "M" were located in column 72 of "L" card, then a title card is prepared wherein all authors' names are given in order.
4-72	69a'	Case (2). Both columns 2 and 3 must be blank. The exact title is placed in columns 4-72 in first and any succeeding title cards if necessary.
73-79	a, 6 ν	Same code is used as for "L" cards.
80	ν	Denotes sequence of title cards. If an author elaboration card (Case 1) is used, a figure 1 is placed in column 80, and all succeeding title cards are numbered in sequence. If no author elaboration card is used (Case 2), the first title card is numbered 1, and the rest numbered in sequence.

6. Comment Cards

For verbal comment storage, column 1 of the card is a C, columns 2 to 8 are a symbol for the comment, column 9 is blank, and columns 10 to 72 are reserved for the comment. This type of card has been used sparingly.

7. <u>Subject File</u>

To avoid disruption of the file of ASM cards, a file arranged according to subjects was developed through the use of a special set of IBM cards. Only selected fields of these cards were coded as follows:

Column	Symbol	Meaning
1	P or M	"P" = pure compound, "M" = mixture.
2-5	$4a$	Property which was investigated. (A list is shown in property codes below.)
22-34	$13\,a'$	Name of compound or material studied.
73-80	$8\,a'$	Usual serial number.

Property codes for the subject file are as follows:

DEBTA	PRO	COMPRESSIBILITY COEFF BETA 1/V DV/DP T
DBIB	PRO	BIBLIOGRAPHY
DCEMP	PRO	CONDENSED PHASE, ELEC OR MAGNETIC PROP, EG WORK FUNC
DCOPT	PRO	CONDENSED PHASE, OPTICAL PROP
DCP	PRO	HEAT CAPACITY
DCRYS	PRO	CRYSTAL STRUCTURE
DCTEX	PRO	COEFF OF THERMAL EXPANSION
DDF	PRO	FREE ENERGY OF FORMATION, REACTION, ETC.
DDH	PRO	HEAT OF FORMATION, REACTION, ETC.
DE	PRO	INTERNAL ENERGY
DELCH	PRO	ELECTROCHEMICAL
DEMF	PRO	ELECTROMOTIVE FORCE

DERES	PRO	ELECTRICAL RESISTIVITY
DF	PRO	FREE ENERGY FUNCTION
DH	PRO	HEAT CONTENT
DKIN	PRO	KINETICS
DMISC	PRO	MISCELLANEOUS
DMSP	PRO	MASS SPECTROMETRIC DATA
DPHAS	PRO	PHASE DATA, MELTING, TRANSITION, BOILING TEMPS
DPMCH	PRO	MECHANICAL PROPERTIES
DREAC	PRO	CHEMICAL REACTIONS
DREV	PRO	REVIEW
DRHO	PRO	DENSITY
DS	PRO	ENTROPY
DSPK	PRO	SPECTROSCOPIC DATA
DTCON	PRO	THERMAL CONDUCTIVITY
DTHEO	PRO	THEORY
DTHER	PRO	THERMODYNAMIC DATA
DVAP	PRO	VAPORIZATION DATA
DZKP	PRO	EQ CONST

8. Definition Cards

a. The usual format for definition cards has been as follows:

Column	Symbol	Meaning
1	D	Definition.
2-6	$2a$, $3a'$	Symbol for the reference.
2-11	REF	Stands for reference.
12	A	An abstracting journal is being coded.
	B	A book is being coded.
	S	A symposium is being coded.
	X	A journal or report number is being coded, and a portion of this number is to be included in the five-character symbol for the reference.
20-72	$53a'$	Definition of journal using abbrevations of Chemical Abstracts and a free field except for books or symposia (see below).

b. For books (designated "B" in column 12), the following pertains:

Column	Symbol	Meaning
21-31	9 α , α	First author, first initial.
32-41	8 α, α	Second author, first initial.
42-63	22 α	Title of book.
64-70	(5α)	Publisher (abbreviated).
71-72	2 ν	Year of publication.

c. For symposia (designated "S" in column 12), the following were used:

Column	Symbol	Meaning
21-31	11 α	Name of town.
32-41	10 α	Name of country.
42-70	29 α	Name of symposium.
71-72	2 ν	Year of meeting.

d. Code-Field Entries

Columns 72-80 of the L-type and certain other cards are called the "code" field. For other fields, symbolic entries have to be defined by definition cards. The interpretation of the code field is too simple to require this, and thus, no "D" cards have been made for code-field entries.

e. Additional Functions of "D" Cards

It is useful to have the "D" cards not only to give the verbal definition of a symbol, but to show relationships between symbols. Thus, the "D" cards become a "thesaurus" as well as a "dictionary." Provision has been made for this in the "D" cards by including an associated symbol field and a control character.

One of the main purposes of the definition cards will be to find duplicate references. Thus, if two ASM cards have been prepared inadvertently from the same original reference, the "code" card will show that this similarity exists. Codes for other methods of using these cards are shown immediately below.

Column	Symbol	Meaning
1	D	Definition.
2-8	α, 6 ν	Symbol for the ASM card to be defined.
9-11	CØD	Code.
12 (usual)	S	Identical (synonymous).
12 (Alternative 12-1)	L	Similar. If a publication had appeared as a journal publication, the contents might be quite similar but not identical.
12 (Alternative 12-2)	T	A translation of basic reference is available.
13-19	α, 6 ν	Symbol for the ASM card in terms of which the entry in columns 2-8 is defined.

f. The following symbol types have become established:

Symbol Type	Meaning
PRØ	Property
UNT	Units
SAG	State of aggregation
WAY	Method of determination
REF	Reference
TBL	Table
MIX	Mixture
CØM	Comment
CND	Condition.

Certain of these symbol types require specification of the A field.

Symbol Type	A Field
UNT	Property measured in these units
WAY	Quantity calculated by this method
CND	Property given by standard state value.

At present, there is only one use for the control character in column 12. S in column 12 means that the symbols in the D and A fields are synonymous. Other control characters can denote other relationships between the D and A fields.

III. CALCULATION AND TABULATION OF THERMODYNAMIC FUNCTIONS FROM AVAILABLE DATA

A. FORMAT AND SCOPE OF TABULATIONS

An important aspect of any project of this type, where thermodynamic functions are to be tabulated, is the format of the tables and the summaries of basic data used in their computation. The standard state reference temperature and the units of numerical data also require careful choice. Standardization in these matters has evolved from a number of such compilations of recent years from the National Bureau of Standards, the Bureau of Mines, etc. A particularly good model for the type of compilation undertaken in this project is that of the JANAF-Thermochemical Panel which is issued under the direction of Dr. D. R. Stull. Except for the introduction of a few innovations, the example of the Thermochemical Panel has been followed in the work on this project so that the results of the two compilations will be compatible. The innovations referred to are the addition of uncertainty estimates and extra entries to define property discontinuities at transition points.

B. STANDARDIZATION OF PHYSICAL AND CHEMICAL CONSTANTS

Another important aspect of data computation and tabulation work is the choice of a consistent set of physical constants such as the atomic weights, gas constants, temperature scales, etc., because more than one atomic weight scale is in general use, and the accepted best value of most constants changes from time to time.

The source of constants (other than atomic weights) selected for this study is the data tabulation by Cohen, Crowe, and Dumond.[1] However, their data have been obtained by reference to the physical atomic scale; whereas for the present work, the chemical atomic scale has been used. The factor for conversion of atomic weights from the physical to the chemical scales was taken as 1.000275 from Birge.[2] Constants converted in this way are given in Table I.

[1] Cohen, E.R., K.M. Crowe, and J.W.M. Dumond, Fundamental Constants of Physics, Interscience, N.Y. (1957), 287 p.

[2] Birge, R.T., Repts. Progr. Phys. 8, 90 (1942).

TABLE I

VALUES OF USEFUL CONSTANTS ON THE PHYSICAL AND CHEMICAL SCALES

Quantity	Physical Scale Value	Chemical Scale Value
Avogadro's number, N	$(6.02486 \pm 0.00016) \times 10^{23}$	$(6.02320 \pm 0.00016) \times 10^{23}$
Gas constant, R_o	1.98780 cal/°K mole	1.98726 cal/°K mole

Wichers[3] has reported the latest status of the atomic weights on the chemical scale, and the table from his paper was used in this work. The authors are unaware of any further changes resulting from the proposed unification of physical and chemical scales by the International Commission on Atomic Weights discussed in Wichers paper.[3]

Some additional constants used in the computations of the project are as follows:

1	Thermochemical calorie (designated "cal" in the tables)	= 4.1840 absolute joules
	e	= 2.7182818284
	$\log_e 10$	= 2.3025850929
	$\log_{10} e$	= 0.4342944819
	$e \times R_o$	= 4.575835 cal/°K mole (chem)
	1 cm^{-1}	= 2.8592696 cal/mole (chem)
	1 erg/molecule	= 1.439584×10^{16} cal/mole (chem)
	1 ev	= 23,062.999 cal/mole (chem)
	Ice Point	= 273.150°K
	hc/k	= 1.43880 ± 0.00007 cm°K.

[3] Wichers, E., J. Am. Chem. Soc. **80**, 4121 (1958).

C. THEORETICAL RELATIONS FOR HEAT CAPACITY VERSUS TEMPERATURE

One of the most important steps in the computation of thermodynamic functions of solids is smoothing and curvefitting of C_p°-versus-temperature data. One looks to the existing theories for mathematical functions to use in this kind of analysis. The theory provides mathematical functions for C_v. C_v and C_p° are almost equal at low temperatures, and these theories are applicable to the data under these conditions. In fact, it may be only at low or moderate temperatures that there is any hope at present for finding suitable mathematical functions for these purposes. This is in no way an attempt at a comprehensive review of the theory but merely at a summary of the best available theories that have direct bearing on the problems of this project. Some comprehensive reviews are available on this subject.[4-8]

1. The Law of Dulong and Petit

An empirical rule that has been often used and quoted is the law of Dulong and Petit,[9] which states that "All solid elements have the same heat capacity per gram atom." At moderate temperatures, the atomic heat capacities are almost constant at 6.2 ± 0.4 cal deg^{-1} in spite of the increase in atomic weight from 7 to 238.[9] In time, it became evident that there were many notable exceptions to this rule, and recent theories have provided a basis for the rule and explanations for the exceptions.

2. Kopp's Law

Kopp's law[9] states that "The molar heat capacity of a solid compound is approximately equal to the sum of the atomic heat capacities of its constituents." This rule has been very useful; for example, it has been used to estimate molecular weights in doubtful cases. Winkelmann's[4, 10] expression for the specific heats of glasses is of the same form.

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[4] Montroll, E.W., Vibrations of Crystal Lattices and Thermodynamic Properties of Solids, In: Handbook of Physics, McGraw-Hill, N.Y. (1958), part 5, chap. 10, p. 159.

[5] Blackman, M., The Specific Heat of Solids. Handbuch der Physik, Springer Verlag, Berlin (1955), p. 325-382.

[6] deLaunay, J., The Theory of Specific Heats of Lattice Vibrations, vol. 2, Solid State Physics, In: Advances in Research and Applications, Academic Press, N.Y. (1956), p. 219-303.

[7] Partington, J.R., An Advanced Treatise on Physical Chemistry, Vol III, Longmans Green, London (1952), p. 264-320.

[8] Born, M. and K. Huang, Dynamical Theory of Crystal Lattices, Oxford Univ. Press, Oxford (1954).

[9] Glasstone, S., Textbook of Physical Chemistry, Van Nostrand, N.Y. (1946), p. 413.

[10] Winkelmann, A., Ann. Physik, 49, 401 (1893).

3. Vibrational Contributions at Low Temperatures

a. Einstein's Theory

The Einstein[5, 11] theory was not completely successful in fitting experimental heat capacities, but the function derived from it is often used in other ways as shall be seen later.

The Einstein model for a crystal system of N identical particles is that each atom vibrates harmonically in the isotropic potential field of all the other atoms. The energy of the particles can be written in terms of three linear harmonic oscillators, one for each dimension in space. The mean energy of a quantum mechanical linear harmonic oscillator with a frequency ν is

$$\bar{\epsilon} = \frac{h\nu}{\exp(h\nu/kT) - 1} \quad . \tag{1}$$

The total energy of the system at equilibrium is therefore $3N\bar{\epsilon}$; and its constant volume heat capacity, obtained by differentiation with respect to temperature, is

$$C_v = 3NkE(x) \, , \tag{2}$$

where

$$x = h\nu/kT \, , \tag{3}$$

and $E(x)$ is the Einstein function,[12]

$$E(x) = \frac{(x/2)^2}{\sinh^2(x/2)} \quad . \tag{4}$$

The limit approached by equation (2) as the temperature increases is 3R per gram atom as it should be, but the limiting form at low temperatures is

$$C_v \cong 3Rx^2 e^{-x} \quad , \tag{5}$$

and this does not fit the low-temperature data of solids very well.

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[11] Einstein, A., Ann. Physik, 22, 180 (1907).

[12] Sherman, J. and R.B. Ewell, A six-place table of the Einstein functions, J. Phys. Chem. 46, 641 (1942).

b. Debye's Elastic-Continuum Theory

Debye[4, 13] was the first to derive a theoretical expression that fitted experimental heat capacities well over the entire range of temperatures for which data existed at that time. It is widely used by itself and in combination with Einstein functions.

Any system of N harmonically coupled point masses has 3N independent, normal modes of vibration with frequencies $\nu_1, \nu_2, \cdots, \nu_{3N}$. The total energy of such a system is

$$E = kT \sum_{j=1}^{3N} x_j \left(\frac{1}{2} - \frac{1}{1 - \exp x_j} \right) , \qquad (6)$$

where

$$x_j = h\nu_j / kT . \qquad (7)$$

C_v is therefore given by

$$C_v = k \sum_{j=1}^{3N} \frac{(x_j/2)^2}{\sinh^2 (x_j/2)} . \qquad (8)$$

For very large values of N, the sum can be approximated by an integral and C_v is given by

$$C_v = k \int_0^{\nu_L} g(\nu) \frac{(h\nu/2kT)^2}{\sinh^2 (h\nu/2kT)} d\nu , \qquad (9)$$

wherein $g(\nu)$ is the frequency distribution function or frequency spectrum, and ν_L is the limiting (largest) or cutoff frequency resulting from the fact that there is a finite number of normal mode frequencies.

[13] Debye, P., Ann. Physik, 39, 789 (1912).

Equation (9) is obviously just an integration of the Einstein function over the distribution function $g(\nu)$.

Debye[13] derived expressions for $g(\nu)$ and ν_L from the theory of vibrations of an elastic continuum.

$$g(\nu) = 4\pi V \nu^2 (2 c_t^{-3} + c_\ell^{-3}) , \tag{10}$$

$$\nu_L = \left[\frac{9N}{4\pi V (2 c_t^{-3} + c_\ell^{-3})} \right]^{1/3} . \tag{11}$$

Therefore, the correct distribution function that allows for the cutoff is

$$g(\nu) = \begin{cases} \dfrac{9N}{\nu_L} \left(\dfrac{\nu}{\nu_L} \right)^2 & \text{if } \nu < \nu_L . \\ 0 & \text{if } \nu > \nu_L . \end{cases} \tag{12}$$

The final expression for C_v is then

$$C_v = 3Nk \left[4D^*(x) - \frac{3x}{\exp(x) - 1} \right] = 3NkD(x) , \tag{13}$$

where the entire function in the brackets is called the Debye specific heat function, $D(x)$,

$$x = \theta_D / T , \tag{14}$$

$$\theta_D = h\nu_L / k , \tag{15}$$

and

$$D^*(x) = \frac{3}{x^3} \int_0^x \frac{\eta^3 d\eta}{e^\eta - 1} \quad . \tag{16}$$

In equation (16), η is a dummy variable, and x is defined by equations (14) and (15). θ_D and $D^*(x)$ are called the Debye temperature and the Debye energy function, respectively. Beattie[14] has tabulated values of the $D(x)$ and $D^*(x)$ functions.

The limiting form of equation (13) at low temperatures; i.e., $x >> 1$, is

$$C_v = 3Nk \left[(4/5)\pi^4 x^{-3} + \cdots \right] \quad . \tag{17}$$

The T^3 function has been extensively used to fit low-temperature heat-capacity data.

The high-temperature limiting form is

$$C_v = 3Nk \left[1 - \left(\frac{1}{20}\right) x^2 + \left(\frac{1}{560}\right) x^4 + \cdots \right] \quad . \tag{18}$$

The limit approached by C_v as the temperature increases is therefore 3R.

Closer examinations of the fit of the Debye theory expression to experimental data have shown that it is not perfect.[5] According to the theory, C_v is a universal function of the temperature with only one adjustable parameter, θ_D. Yet the value of θ_D is found to be a function of the temperature for all substances.[5] Improvement of the theory has been sought in sophisticated studies of the discrete lattice.[8]

c. Conclusions from Discrete Lattice Theory

It is only natural that attempts would be made to improve the fitting of experimental data by employing combinations of Einstein and Debye functions. The Nernst-Lindemann[15] formula,

[14] Beattie, J.A., J. Math. Phys. 16, 1 (1926).

[15] Nernst, W. and F.A. Lindemann, Z. Elektrochem; 17, 817 (1911).

$$C_v = \left(\frac{3Nk}{2}\right)\left[E(x) + E(x/2)\right] , \qquad (19)$$

is an example which fitted some data well because the vibrational spectra happened to contain two peaks, one at roughly one half of the frequency of the other.[5, 16] Wise et al[17] have recently employed the formula,

$$C_p^o/R = D(\theta_D/T) + 2E_1(\theta_1/T) + E_2(\theta_2/T) , \qquad (20)$$

to represent their boron data where the significance of the subscripts 1 and 2 on E_1 and E_2 was not explained. This must be regarded as an arbitrary curve-fitting procedure since it is not applied to C_v, it leads to a high temperature limit of 4R for C_p^o, and it neglects contributions from anharmonicity corrections as well as the $9\beta^2 VT/\kappa$ term to be discussed later.

Sophisticated theories of the discrete lattice[8, 18] have provided a rational basis for this type of approach. For a lattice containing s atoms per unit cell, it has been deduced that there are 3s solutions to the secular equations for the angular frequency. Three solutions (acoustic branches) tend to $\omega = 0$ as the wavelength approaches infinity; $3s - 3$ solutions (optic branches) tend to ω = constant as the wavelength approaches infinity.

An important approximation has been obtained by application of the following assumptions:

1) The optical branches are considered to contain a narrow range of frequencies, and the specific heat contribution of each is approximated by an Einstein function ("i" summation index).

2) The acoustic branches are each represented by a Debye spectrum with a suitable Debye temperature. ("j" summation index).

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[16] Blackman, M., Proc. Roy. Soc. (London), A148, 384 (1935).

[17] Wise, S., J.L. Margrave, and R.L. Altman, The heat content of boron at high temperatures, J. Phys. Chem. 64, 915 (1960).

[18] Born, M., Atomtheorie des festen Zustandes (1923).

Therefore, the heat capacity for a gram formula weight of the s atoms is

$$C_v^s = R \sum_{j=1}^{3} D(\bar{\theta}_j/T) + R \sum_{i=4}^{3s} E(\bar{\theta}_i/T) \quad . \tag{21}$$

$D(\bar{\theta}_j/T)$ is the Debye specific heat function (in Eq. (13)), and $E(\bar{\theta}_i/T)$ is the Einstein function (Eq. 4).

The $\bar{\theta}_j$ must be chosen so that C_v fits the data well at low temperatures (where the acoustic branches are important), and the corresponding average velocities satisfy the relation,

$$\frac{1}{\bar{c}_j^3} = \int \frac{1}{c_j^3} \frac{d\Omega}{4\pi} \quad , \tag{22}$$

for each acoustic branch where Ω is the solid angle. This is necessary since the velocities can be orientation-dependent and the frequency spectrum, in the limit of low frequencies, is $3\ VF\ \nu^2$, where

$$F = (4\pi/3) \int \sum_{j=1}^{3} \left(\frac{1}{c_j^3}\right) \frac{d\Omega}{4\pi} \quad . \tag{23}$$

The quantity F corresponds to $(2c_t^{-3} + c_\ell^{-3})$ in the Debye theory. Values of $\bar{\theta}_j$ for the acoustic branches can be estimated from the elastic constants of the solid since

$$\bar{\theta}_j = \left(\frac{h}{k}\right) \bar{\nu}_j = \left(\frac{h}{k}\right) \bar{c}_j \left(\frac{3}{4\pi V_a}\right)^{1/3} \quad , \tag{24}$$

where $\bar{c}_j$ is the average sonic velocity for each branch, and V_a is the volume of the unit cell. The average velocity can be calculated directly using the determinant for the velocity of propagation of elastic waves from the standard theory of elasticity of solids. This determinant provides an equation relating c_j to the lattice parameters and the direction of propagation which makes it possible to evaluate the integral in equation (22) and obtain the average velocity $\bar{c}_j = \sqrt[3]{\bar{c}_j^3}$. The optical frequencies ν_4 to ν_{3s} can be taken as the frequencies where the solid shows minimum transmission in the infrared.

The limit approached by equation (21) as the temperature increases is 3Rs for a gram formula weight of the s atoms. The average limiting heat capacity per gram atom is therefore the classical value 3R.

Equation (21) applies best where the acoustic and optical branches are well separated. When they are not well separated, it may give a worse fit than a single Debye spectrum.[5]

In trying to obtain a fit to low-temperature data by simultaneous solution with 3s points, one should remember that the points must be "smoothed" since the raw data contain statistical variations within their accuracy limits. This method should be used in combination with a least-squares regression analysis to obtain the most probable values of the $\bar{\theta}_j$'s and $\bar{\theta}_i$'s.

Detailed calculations of frequency spectra have been made for several systems such as a body-centered cubic lattice (fitted to the tungsten elastic constants[19]), ionic crystals of the alkali halide type[20] (characterized by long-range coulombic forces between ions), diamond,[21] face-centered (close-packed) cubic crystals,[22] and alkali metals.[23] In general, these frequency spectra have a form not in good agreement with the assumptions in equation (21). Debye spectra do not generally represent the acoustic branches well. In the case of ionic crystals, there is a pronounced, high-frequency tail to the optic branches that makes the use of Einstein functions dubious. However, one must bear in mind that the heat capacity is rather insensitive to the form of the frequency spectrum, especially at very high temperatures, and crude approximations in $g(\nu)$ can give surprisingly useful representations of the harmonic vibration contributions to C_v.

[19] Fine, P.C., Phys Rev. 56, 355 (1939); Montroll, E.W. and D. Peaslee, J. Chem. Phys. 12, 98 (1944).

[20] Kellermann, E.W., Phil. Trans. Roy. Soc. (London) 238A, 513 (1940); Jona, M., Phys Rev. 60, 823 (1941).

[21] Smith, H., Phil. Trans. Roy. Soc. (London) 241A, 105 (1948).

[22] Leighton, R.B., Rev. Mod. Phys. 20, 165 (1948).

[23] Fuchs, K., Proc. Roy. Soc. (London) 157A, 444 (1936).

A number of methods have been worked out for obtaining Debye temperatures from other physical properties,[5] such as the temperature dependence of the intensity of X-ray diffraction spots, infrared absorption or reflection peaks, compressibilities, melting points, electrical resistance, and expansion coefficients. Such methods provide only crude estimates of C_v at low or moderate temperatures because of the inadequacy of a single Debye temperature in fitting actual data. Moreover, the Debye temperatures so obtained do not exactly equal those obtained directly from C_v data at any temperature. The "thermal spot" theory appears to offer some promise since it can be used to obtain detailed frequency spectra indirectly from lattice constants derived from studies of X-ray scattering.[5]

4. Electron Gas Contributions at Very Low Temperatures

The free electron gas in electrical conductors is responsible for most of their heat capacity at very low temperatures.[4] The free electrons obey Fermi-Dirac statistics, and this results in a low-temperature heat capacity contribution proportional to the absolute temperature. When combined with equation (17), this results in the expression often used with metals at very low temperatures

$$C_p^\circ = 464.4\,(T/\theta_D)^3 + \alpha T \,. \tag{25}$$

The electron gas contribution is negligible at the intermediate temperature level.

5. High-Temperature Specific Heat of Solids

Some progress has been made in the development of the theory of specific heats of solids at high temperatures[5, 24, 25] but more progress needs to be made in calculations for individual systems before our understanding of this property is complete.

Experimental measurements provide C_p° data, but the theory is usually concerned with C_v . These two quantities are related by means of the well-known equation derived from rigorous thermodynamic relations i.e.

$$C_p^\circ = C_v + 9\beta^2 VT/\kappa \,, \tag{26}$$

[24] Born, M. and E. Brody, Z. Physik 6, 132 (1921).

[25] Schroedinger, E., Z. Physik 11, 170 (1922).

TABLE II

REPRESENTATIVE HIGH-TEMPERATURE HEAT CAPACITY DATA

Number of Atoms	Element or Compound	T °F	T °K	C_p^o cal/gfw°C	Reference Number	C_p^o/s cal/gfw°C
2	TiC	2800	---	13.180	26	6.59
2	TiN	2800	---	13.496	26	6.75
2	TiN	4000	---	14.2	27	7.1
3	ThO_2	---	2000	22.40	26	7.47
2	MgO	3200	---	13.669	26	6.83
2	BN	1700	---	8.207	26	4.10
2	BeC	2800	---	7.022	28	3.51
2	BeO	1400	---	12.256	26	6.13
1	Graphite	2000	---	5.405	26	5.404
1	ATJ Graphite	4000	---	5.5	29	5.5
1	Graphite	3125	---	5.92	This Project	5.92
1	Graphite	3040	---	5.94	27	5.94
3	UO_2	2200	---	21.330	26	7.11
3	TiO_2	2800	---	13.496	26	4.50
4	UCl_3	1400	---	31.682	30	7.92
2	ZrN*	4000	---	12.6	29	6.3
5	Zr_3N_2	975	---	42.235	26	8.46
5	Al_2O_3	2800	---	32.627	26	6.53
5	Al_2O_3	---	1873-2273	38.2	31	7.65
5	Cr_3C_2	1790	---	37.811	26	7.56
1	W	---	1273	6.66	7	6.66
1	W	4000	---	7.7	29	7.7
1	Fe-γ	---	1773	9.44	7	9.44
1	Fe-α	---	773	9.10	7	9.10
1	Fe-α	---	973	12.84	7	12.84
1	Fe-α	---	1073	11.70	7	11.70
1	B	---	2000	7.288	17	7.288
1	B	---	2000	7.20	32	7.20
7	Si_3N_4*	4000	---	42.1	29	6.0
2	TaB*	4000	---	18.8	29	9.4
2	ZrC*	4000	---	12.4	29	6.2
2	NbC*	4000	---	13.1	29	6.6
2	TaC*	4000	---	13.9	29	7.0
2	ZrB*	4000	---	18.4	29	9.2

*Assumed formula; not given by source.

[26] Kelly, K.K., Data on Theoretical Metallurgy, X. High Temperature Heat Content and Entropy for Inorganic Compounds, U.S.Bur. Mines Bull. 476 (1949).

[27] Rasor, N.S. and J.D. McClelland, Part I. Thermal Properties of Materials, Properties of Graphite, Molybdenum and Tantalum to Their Destruction Temperatures WADC-TR-56-400 (1956).

[28] Ginnings, D.C. and G.T. Furukawa, Heat capacity standards for the range 14° to 1200°K, J. Am. Chem. Soc. 75, 525 (1953).

[29] Southern Research Institute, Quarterly Progress Report No. 4 to WADD, Rept. No. 4398-1068-XII, The Thermal Properties of Solid Materials to Very High Temperatures, Contract AF33(616)-6312 (8 April 1960).

[30] Ginnings, D.C. and R.J. Corruccini, An Improved Ice Calorimeter - The Determination of Its Calibration Factor and The Density of Ice at 0°C, J. Research Nat. Bur. Stds. 38, 583 (1947).

[31] Kirillin, V.A., A. YeSheyndlin, and V. YaChenkovskiy, Akademiya nauk SSSR, Doklady, 135, 125 (1960).

[32] Sinke, G.C., D.R. Stull, R.M. Hunter, H.A. Robinson, and R.P. Ruh, Thermodynamic Properties of Combustion Products, WADC and ARPA, Rept. AF-214-587, Dow Chem. Co. (1 April 1959).

where β is the linear thermal expansion coefficient, V is the volume, and κ is the bulk compressibility.* The first term on the right takes care of the vibrational energy contributions and approaches a high-temperature limit of 3R per gram atom for a harmonically vibrating lattice. The second term on the right accounts for the energy absorbed due to expansion against the cohesive forces of the solid.

In many actual cases, as one can see from Table II, the 3R limit per average gram atom is exceeded at high temperatures, and one must look for large contributions from the expansion term and other possible terms due to anharmonicity, conduction electrons, gradual transitions, and higher electronic energy levels. The extensive heat capacity data for tungsten[33] plotted in figure 2 show how these additional contributions and the expansion term vary with temperature for that substance.

a. Constant Volume (Vibrational) Heat Capacity Contribution

Born and Brody[24] and Schroedinger[25] investigated the specific heat of an anharmonically vibrating lattice. Born and Brody approached the problem by studying the contributions of terms higher than quadratic in the displacement coordinates of the potential energy to the Helmholtz free energy of a system of quantum mechanical oscillators at large amplitudes. From this, they calculated corresponding contributions to the entropy and internal energy and obtained those for C_v by differentiation of the latter with respect to temperature. They found the limiting form of C_v at high temperatures to be

$$C_v = 3R(1-6\sigma RT) \tag{27}$$

From equation (27), it can be seen that the anharmonicity correction over the classical limiting value is $-18\sigma R^2T$. σ is a characteristic constant of the crystal whose sign is thought by some to be not determined so that it could presumably be either positive or negative.[5,7] Born and Brody[24] state that σ is negative and that C_v values above 3R are to be expected.

The case of rocksalt has been analyzed by two methods,[34, 35] and there appears to be a maximum in C_v versus temperature of uncertain validity. There is no evidence for such a maximum in the tungsten[33] data in figure 2. It is also obvious from the figure that harmonic vibration contributions do not account for the value of C_v at high temperatures. The difference between C_v and 3R at high temperatures is large and not quite linear with temperature.

[33] Zwikker, C. and G. Schmidt, Physica, 8, 329 (1928).

[34] Eucken, A. and W. Dannöhl, Z. Elektrochem. 40, 814 (1934).

[35] Siegel, S. and L. Hunter, Phys. Rev. 61, 84 (1942).

*$\beta = (1/\ell)(\partial \ell/\partial T)_p$ and $\kappa = -(1/V)(\partial V/\partial p)_T$ where ℓ is length and p is pressure.

It is possible in principle to calculate C_v for ionic crystals, using the free energy, by a method developed by Born.[36]

b. The Expansion Term

Euken and Dannohl[34] have made an analysis of $C_p^\circ - C_v$ for a number of substances relying upon the assumption that the Gruneisen constant γ is independent of temperature to obtain the compressibility from the thermal expansion coefficient. In the case of rocksalt, the results of their analysis differ enough from those of Siegel and Hunter,[35] who used a complete set of available data, that the method must be considered with some reservations. Siegel and Hunter found that the $9V\beta^2T/\kappa$ term is large at high temperatures.

Gruneisen's[4, 37, 38] theory for the equation of state of a solid neglects anharmonicities. This theory assumes that the normal mode frequencies are volume- or lattice-spacing-dependent. This dependence is represented by a parameter γ, the Gruneisen constant. The equation of state and expansion coefficients are therefore functions of γ. For the well-known Debye continuum model of a crystalline solid, γ is defined as

$$\gamma = - \frac{\partial \log \theta_D}{\partial \log V} , \tag{28}$$

where θ_D is the Debye temperature, and V is the volume. From the equation of state of a Debye crystal, one finds that

$$(\partial p/\partial T)_V = \gamma C_v/V , \tag{29}$$

and

$$\beta = \kappa \gamma C_v/3V , \tag{30}$$

since

$$\beta = (1/3)\kappa(\partial p/\partial T)_V . \tag{31}$$

[36] Born, M., J. Chem. Phys. 7, 591 (1939).

[37] Gruneisen, E., Handbuch der Physik, vol. 10, p. 22, Springer-Verlag, Berlin (1953).

[38] Slater, J.C., Introduction to Chemical Physics, McGraw-Hill, N.Y. (1939), p. 215-220.

This provides a useful approximation for evaluating the expansion term $9V\beta^2T/\kappa$ in equation(26). γ for many metals remains constant over a wide range of temperatures and densities.

Lindemann and Magnus[9] proposed the empirical equation,

$$C_p^\circ - C_v = aT^{3/2} , \tag{32}$$

wherein a is a different constant for each substance. Since this formula, with a equal to 7×10^{-6} cal $°K^{-5/2}/g$ atom, fits the tungsten data in figure 2 within a few tenths of a cal/g atom °K, it appears to be a useful approximation for use in extrapolating rough data. A more exacting test of this approximation is presented in figure 3 which shows more precisely the extent of accuracy that can be expected.

c. Conduction Electron Contributions

For the heat capacity of electrical conductors such as metals, there is a contribution proportional to the temperature for the conduction electrons at low temperatures as discussed in section III-C4.[4] This contribution is negligibly small for most metals at room temperature except for the transition elements such as platinum and palladium.[5] Since this contribution is an increasing function of the temperature, it could well contribute outside the experimental error at very high temperatures for many refractory metals. Many of the compounds within the scope of this project become conductors at high temperature, but the importance of this contribution to their heat capacity is unknown.

The large contribution in the case of ferroelectric metals has been discussed in some detail.[39, 40, 41]

d. Transitions

The occurrence of thermal transitions complicates the analysis of high-temperature specific heat data even further. These can be of several types which in principle can be clearly classified but in practice are less definite. A brief but penetrating review of this subject has been provided by Smoluchowski.[42]

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[39] Stoner, E.L., Proc. Roy. Soc. (London) A169, 339 (1939).

[40] Mott, N.F., Proc. Roy. Soc. (London) A152, 43 (1935).

[41] Hunt, E.L., Proc. Roy. Soc. (London) A216, 103 (1953).

[42] Smoluchowski, R., Phase Transformations in Solids, In: Handbook of Physics, McGraw-Hill, N.Y. (1958), Chap. 8, p. 8-108.

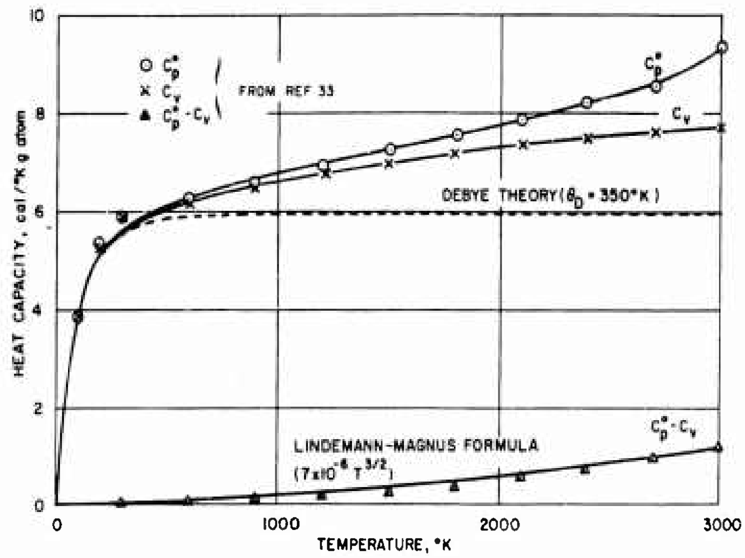

Figure 2 ATOMIC HEAT CAPACITY OF TUNGSTEN VERSUS TEMPERATURE

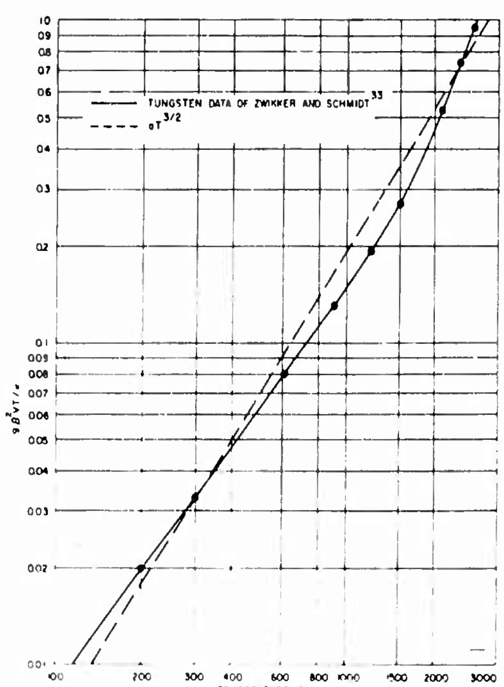

Figure 3 TEST OF LINDEMANN-MAGNUS FORMULA WITH TUNGSTEN DATA

Ehrenfest suggested a classification of transitions into orders according to which a transition is of the n^{th} order when temperature derivatives of F, the free energy, lower than the n^{th} are continuous at the transition temperature while the n^{th} derivative is discontinuous. Strictly speaking, only first-order transitions are phase transformations, but this designation has been commonly used for all transitions.

The usefulness of Ehrenfest's classification has been limited because of various intermediate kinds of anomalies that make it difficult to determine whether or not continuity of thermodynamic functions exists. Figure 4, due to Mayer and Streeter,[43] illustrates various common types of transformations.

First-order transformations are in principle simple to treat. They are the most common type where two phases can coexist in equilibrium and there is a definite heat of transformation. Integrations for thermodynamic functions can be performed smoothly over the two separate phases on either side of the transition point, and a heat and an entropy of transition can be added above the transition temperature, the free energy of transition being zero. Often in practice however, each phase anticipates the onset of the other so that the transition is not perfectly sharp. Large rises in C_p^o just below the melting point, called premelting, have been observed.

Second-order transformations are usually of the "lambda" type. In such cases, some continuous change is evident, and a definite heat of transformation cannot be assigned.

Diffuse transformations are spread out over a large range of temperature. Here again a definite heat of transformation cannot be assigned to them.

Certain crystals such as ammonium and hydrogen halides undergo a transformation as the temperature is increased that was first thought to be due to the onset of free rotation.[44] A better interpretation appears to be that of Frenkel,[45] who proposes that it corresponds to a progressive decrease in orientation of oscillation axes of the ions up to a critical temperature and then random orientation above the critical temperature.[46, 47, 48] How generally this type of transformation

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[43] Mayer, J.E. and S.F. Streeter, J. Chem. Phys. 2, 1019 (1939).

[44] Pauling, L., Phys. Rev. 36, 430 (1930).

[45] Frenkel, J., Acta Physiochem. (USSR) 3, 23 (1935).

[46] Wagner, E.L. and D.F. Hornig, J. Chem. Phys. 18, 296 (1950).

[47] Levy, H.A. and S.W. Peterson, Phys. Rev. 83, 1270 (1951).

[48] Lawson, A.W., Phys. Rev. 57, 417 (1940).

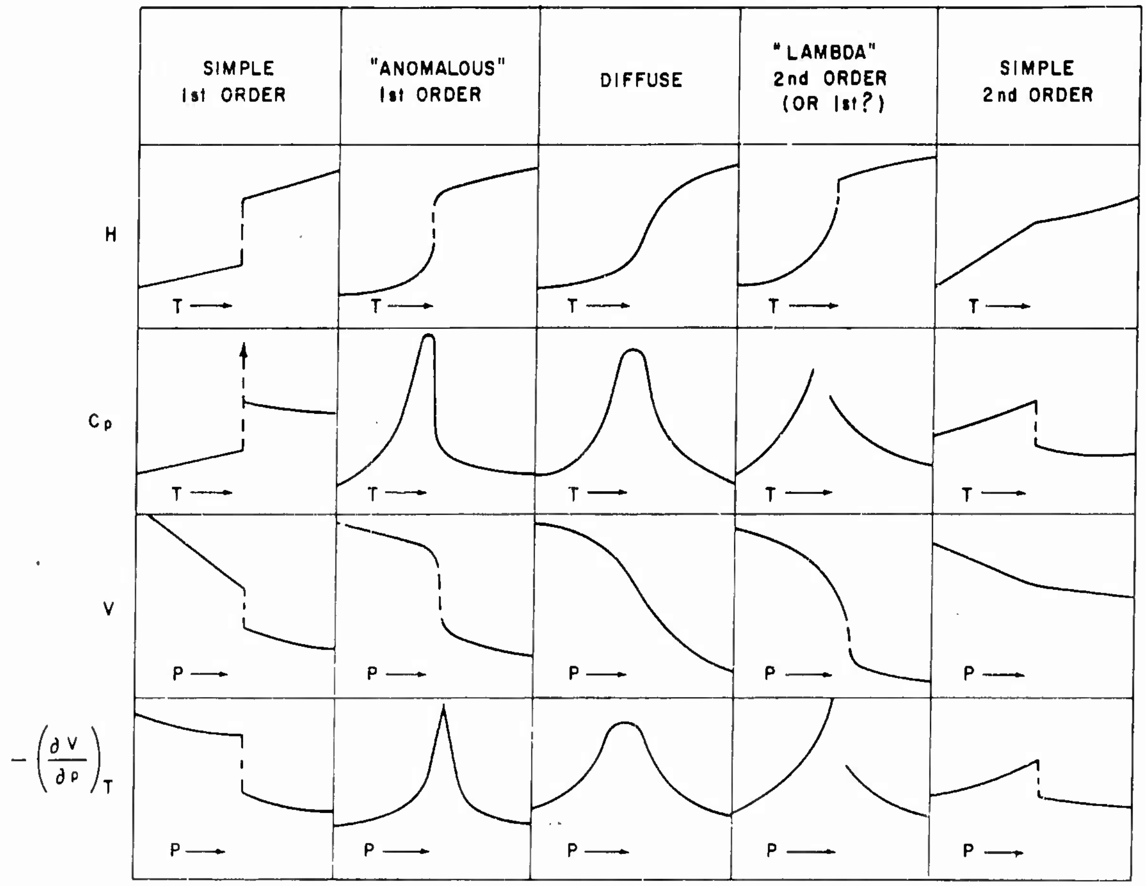

Figure 4 TYPES OF TRANSFORMATIONS IN SOLIDS

occurs is not known, but a similar type has been reported to occur in many organic compounds and even polymers.[49]

Another phenomenon which appears in many metals and compounds at very high temperatures is thermionic emission. This also cannot strictly speaking be considered a transformation since it develops gradually as the temperature is increased. Its importance to the thermodynamic properties of the solid depends upon the extent to which it occurs which in turn depends upon the work function. Since it provides an electron gas species in the vapor at equilibrium with the solid, it is related to the ionic equilibria in the vapor.

[49] Glasstone, S., op. cit., p. 428.

D. THE MONATOMIC GAS COMPUTER PROGRAM

1. Method of Calculation

The methods of calculation for the thermodynamic properties of monatomic gases are well known and have been described in many standard texts, articles, reports, etc.[50, 51] The general procedure followed in the present project has been that of Kolsky, Gilmer, and Gilles.[51] Their equations were modified in some cases to give the following formulas adopted for use in the present work:

$$Q = \sum_i (2J_i + 1)\, e^{-\frac{a\nu_i}{T}} , \tag{33}$$

$$Q_1 = \sum_i (2J_i + 1)\, \nu_i\, e^{-\frac{a\nu_i}{T}} , \tag{34}$$

$$Q_2 = \sum_i (2J_i + 1)\, \nu_i^2\, e^{-\frac{a\nu_i}{T}} , \tag{35}$$

$$H^\circ_{298} - H^\circ_0 = K_1 \left(\frac{Q_1}{Q}\right)_{298} + 298.15\, K_2 , \tag{36}$$

$$H^\circ_T - H^\circ_{298} = K_1 \left[\left(\frac{Q_1}{Q}\right) - \left(\frac{Q_1}{Q}\right)_{298}\right] + K_2\, \frac{(T - 298.15)}{1000} , \tag{37}$$

$$C^\circ_P = \frac{K_3}{T^2}\left[\left(\frac{Q_2}{Q}\right) - \left(\frac{Q_1}{Q}\right)^2\right] + K_2 , \tag{38}$$

$$S^\circ_T = \frac{K_1}{T}\left(\frac{Q_1}{Q}\right) + R \ln Q + K_4 \ln M + K_2 \ln T + K_5 , \tag{39}$$

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[50] Mayer, J. E. and M. G. Mayer, Statistical Mechanics, Wiley, N.Y. (1940), p. 109.

[51] Kolsky, H. G., R. M. Gilmer, and P. W. Gilles, The Thermodynamic Properties of 54 Elements Considered As Ideal Monatomic Gases, Los Alamos Scientific Laboratory, Rept. LA-2110 (15 March 1957).

$$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right) = R \ln Q + K_4 \ln M + K_2 \ln T + K_6 + \frac{K_1}{T}\left(\frac{Q_1}{Q}\right)_{298}$$

$$+ K_2 \left(\frac{298.15}{T}\right) , \tag{40}$$

$$-\left(\frac{F_T^\circ - H_O^\circ}{T}\right) = R \ln Q + K_4 \ln M + K_2 \ln T + K_6 \quad ,$$

$$-\left(\frac{F_T^\circ - H_O^\circ}{T}\right) + \left(\frac{H_{298}^\circ - H_O^\circ}{T}\right) = -\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right) \quad , \tag{41}$$

$$\Delta H_f^\circ = \Delta H_{f298}^\circ + (H_T^\circ - H_{298}^\circ)_{\text{monatomic gas}} - (H_T^\circ - H_{298}^\circ)_{\text{ref. state}} \quad , \tag{42}$$

$$\Delta F_f^\circ = \Delta H_{f298}^\circ - \frac{T}{1000}\left[-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)_{\text{monatomic gas}}\right.$$

$$\left. + \left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)_{\text{ref. state}}\right] , \tag{43}$$

$$\text{Log}_{10} K_p = \frac{-1000 \, \Delta F_f^\circ}{4.575835 \, T} \tag{44}$$

Definitions of some of the symbols used above can be found in Table III. The remainder are defined as follows:

Q = partition function,

J_i = inner quantum number of the ith state,

ν_i = wave number for a given energy level in cm^{-1},

T = absolute temperature in degrees Kelvin,

$H_{298}^\circ - H_O^\circ$ = enthalpy of an ideal gas at 298.15°K relative to the ideal gas at absolute zero,

TABLE III

VALUES OF PHYSICAL CONSTANTS FOR GAS-PHASE CALCULATIONS

Constant	Definition	Value of Kolsky et al[51]	Units	Value Used in Present Work	"Perturbed" Value Used in Error Calculation
a	$\frac{hc}{k}$	1.43880	cm deg	1.43880 ±0.00007	1.43873
K_1	Ra	2.860047	cal cm $mole^{-1}$	2.8592696 ±0.000254	2.859523
K_2	$(5/2)R$	4.96950	cal $deg^{-1}mole^{-1}$	4.968150 ±0.00020	4.968350
K_3	Ra^2	4.115035	cal cm^2deg $mole^{-1}$	4.1139163 ±0.000565	4.114481
K_4	$(3/2)R$	2.98170	cal $deg^{-1}mole^{-1}$	2.98089 ±0.00012	2.98101
K_5	Sackur-Tetrode Constant[20]	-2.316818	cal $deg^{-1}mole^{-1}$	-2.315380 ±0.00013	-2.31525
K_6	$K_5 + (5/2)R$	-7.286318	cal $deg^{-1}mole^{-1}$	-7.283530 ±0.00033	-7.28320
R	Gas Constant	1.98780	cal $deg^{-1}mole^{-1}$	1.98726 ±0.000081	1.98734

$H^\circ_T - H^\circ_{298}$ = enthalpy of an ideal gas at temperature T , relative to the ideal gas at 298.15°K.

C°_p = heat capacity of ideal gas in cal/°K, g mol,

S°_T = entropy of ideal gas in cal/°K, g mol,

$-\left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)$ = free-energy function, in cal/°K, g mol,

M = molecular weight,

R = gas constant, cal/°K g mol,

ΔH°_f = standard heat of formation at temperature T, in Kcal/g mole,

ΔH°_{f298} = standard heat of formation at 298.15°K, in Kcal/g mole,

ΔF°_f = standard free energy of formation at temperature T, in Kcal/g mole,

K_p = equilibrium constant for sublimation or vaporization to a monatomic gas from the condensed phase of the pure element.

The values of the constants used in these equations were based on the work of Cohen, Crowe, and Dumond.[1] The derived constants for the above equations are listed in Table III. For the sake of comparison, the constants used by Kolsky et al[51] were also included. It should be noted that their value of the gas constant was based on the physical atomic weight scale, whereas the value based on the chemical atomic weight scale has been adopted in the fifth column of the table. All derived quantities were therefore correspondingly adjusted. The uncertainties in the fifth column were derived from the values of Cohen, Crowe, and Dumond.[1]

The machine program used for preparing ideal monatomic gas tables containing C°_p, S°_T, $-\left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)$, $H^\circ_T - H^\circ_{298}$, ΔH°_f, ΔF°_f, and $\mathrm{Log}_{10} K_p$ was based on the equations summarized above. The required input data for its use are:

a. J_i versus ν_i (cm^{-1}),

b. The eight constants in the last two columns of Table III,

c. The molecular weight on the chemical scale,

d. ΔH°_{f298} in Kcal/mole,

e. Enthalpy of the reference state as a function of temperature,

f. Free energy of the reference state as a function of temperature,

g. The temperature for each entry of the table.

2. <u>Uncertainty-Range Calculations</u>

The uncertainty limits were obtained by repeating the calculation described immediately above with the "perturbed" values in the last column of Table III and individually chosen values of the other input data. The difference between the results of the two calculations was taken as the uncertainty range.

Considerable thought had to be given to the choice of the other input data for the uncertainty analysis. This is worthwhile to discuss in more detail.

a. J_i versus ν_i

The ν_i values were obtained by a "perturbation" of the last significant figure given in Moore's tables;[52] i.e., the ones used in the normal calculation above. For example, if ν_i = 16 cm^{-1} as reported by Moore, then the perturbation was -1, giving $\nu_{i(\text{perturbed})}$ = 15 cm^{-1}. A negative "perturbation" was used since this should lead to an increased occupation of excited levels at a given temperature, as compared with the "unperturbed" states.

This means that the partition function (and consequently, the free-energy function) was maximized. Since the free-energy function is basically the most important single thermochemical quantity with the exception of the heat of formation, it is seen that this procedure is the optimum one. However, if desired, a positive perturbation could also be used, and the calculations repeated.

[52] Moore, C. E., Atomic Energy Levels, NBS Circular 467, vol. 1 (15 June 1949).

b. The Eight Constants of Table III

The constants in Table III were "perturbed" from the "best" values in the fifth column, again in such a manner as to maximize the errors in the free-energy function.

c. The Molecular Weight on the Chemical Scale

Normally, no perturbation was included for the molecular weight, but this could be included if the uncertainties in molecular weight became appreciable. For example, if the uncertainty in molecular weight became 1 part in 2500, an error of about 0.001 e.u. could be assigned to S°_T or the free-energy function.

d. ΔH°_{f298} in Kcal/mole

Errors in ΔH°_{f298} are ordinarily the largest and most significant in thermodynamic calculations. These errors will lead to errors in ΔH°_f, ΔF°_f, and $\mathrm{Log}_{10} K_p$. The input to the calculation routine described above consisted of the absolute value of the uncertainty, designated a_{298}. This is equivalent to considering the true value of ΔH°_{f298} to lie in the range of $\Delta H^\circ_{f298} \pm a_{298}$.

e. Uncertainties in Enthalpy Functions

Uncertainties in the enthalpy functions of the monatomic gas were labeled b_T (Kcal/gram atom of gas). Thus, $(H^\circ_T - H^\circ_{298})$ was considered to be within the range of values of $(H^\circ_T - H^\circ_{298}) \pm b_T$. Values of b_T were taken from results of the calculation based on the data in steps (a) through (c) above.

Uncertainties in the enthalpy functions of the reference state were labeled c_T and fed into the program as input data.

f. Uncertainties in Free-Energy Functions

Uncertainties in the free-energy functions of the monatomic gas and reference state were designated as d_T and e_T, respectively. They were obtained in the same manner as b_T and c_T described just above.

g. Uncertainties in ΔH°_f, ΔF°_f, and $\mathrm{Log}_{10} K_p$

The uncertainties in ΔH°_f, ΔF°_f, and $\mathrm{Log}_{10} K_p$ were obtained as the sum of the component uncertainties since each term in the summation is independent of any other. For example, since

$$\Delta H_f^\circ \pm \delta \Delta H_f^\circ = (\Delta H_{f298}^\circ \pm a_{298}) + \left[(H_T^\circ - H_{298}^\circ)_{gas} \pm b_T\right]$$

$$- \left[(H_T^\circ - H_{298}^\circ)_{ref} \pm c_T\right] \quad , \tag{45}$$

then,

$$\delta (\Delta H_f^\circ) = a_{298} + b_T + c_T \quad . \tag{46}$$

Likewise, the other uncertainties are

$$\delta (\Delta F_f^\circ) = a_{298} + \frac{T}{1000} (d_T + e_T) \quad , \tag{47}$$

and

$$\delta (\mathrm{Log}_{10} K_p) = \left[\delta (\Delta F_f^\circ)\right] \left[\frac{1000}{4.575835\ T}\right] \quad . \tag{48}$$

E. DIATOMIC MOLECULE CALCULATIONS

The computer program used in the calculations of the thermodynamic functions of diatomic molecules was based on a treatment of the diatomic molecule developed by Mr. T. Munson of Avco RAD over a period of time. A program for a single electronic state using this treatment has been in use on other projects at Avco RAD. The present program was designed to be applied to the general case of the diatomic molecule with multiple electronic states. The following discussion of the calculation is based on the standard equations and symbols of the spectroscopists, except where duplications of symbol usage might result in confusion.

The treatment of a given electronic state is an elaboration of the method of Mayer and Mayer[50] but takes into account spectroscopic constants of higher order than the latter.

The input data for the program are the electronic energy (defined later) and the standard spectroscopic constants ω_e, $\omega_e x_e$, $\omega_e y_e$, B_e, α_e, γ_e, and D_e. Although values of γ_e are not commonly tabulated, they may be estimated from Dunham's equations.[53] Spectroscopic constants which are sometimes determined but which are not included in the present calculation are $\omega_e z_e$, β_e, and coefficients of powers of γ $(\gamma + 1)$ greater than the second.

It is assumed that the internal energy, exclusive of the electronic energy, may be expressed as a function of the quantum numbers v and j for a given electronic state by the expression

$$\epsilon_i = \omega_e\left(v + \frac{1}{2}\right) - \omega_e x_e\left(v + \frac{1}{2}\right)^2 + \omega_e y_e\left(v + \frac{1}{2}\right)^3$$

$$+ j(j+1)\left[B_e - \alpha_e\left(v + \frac{1}{2}\right) + \gamma_e\left(v + \frac{1}{2}\right)^2\right] - D_e j^2 (j+1)^2 , \qquad (49)$$

where the energy is expressed in wave numbers.

If the energy of the lowest level ($v = 0$, $j = 0$) is taken as zero, equation (49) may be re-arranged and put in the form

$$(\epsilon - \epsilon_0)_i = \omega v - \omega x v(v-1) + \omega y v(v-1)(v-2)$$

$$+ j(j+1)\left[1 - \rho j(j+1) - (\delta - \phi)v - \phi v^2\right] B_e(1 - \delta/2) , \qquad (50)$$

[53] Dunham, J.L., Phys. Rev. 41, 721 (1932).

where

$$\omega = \omega_e - 2\,\omega_e x_e + (13/4)\,\omega_e y_e\,,$$

$$\omega x = \omega_e x_e - (9/2)\,\omega_e y_e\,,$$

$$\omega y = \omega_e y_e\,,$$

$$x = \omega x/\omega\,,$$

$$y = \omega y/\omega\,,$$

$$\rho \cong D_e/B_e\,, \tag{51}$$

and the following definitions are added

$$\delta = \alpha_e/B_e + (\alpha_e/B_e)^2 - 2\gamma_e/B_e\,,$$

$$\phi = -\gamma_e/B_e + \frac{1}{2}(\alpha_e/B_e)^2\,. \tag{52}$$

In arriving at the above definitions, it is convenient to use the approximation

$$\gamma_e \cong (2/3)\,\alpha_e^2/B_e\,, \tag{53}$$

which follows from Dunham's equations.[53]

The internal partition function, exclusive of a term for the electronic energy, may be written as

$$Q(v,j) = \sum_{v,j}(2j+1)\exp\Big\{-u\Big[v - xv(v-1) + yv(v-1)(v-2)\Big] - \sigma j(j+1)\Big[1 - \rho j(j+1) - (\delta-\phi)v - \phi v^2\Big]\Big\} = \frac{Q_c}{\sigma(1-e^{-u})}\,, \tag{54}$$

where $1/\sigma$ is the partition function for the rigid rotator, $1/(1 - e^{-u})$ is the partition function for the harmonic oscillator, and Q_c contains the terms for anharmonicity and rotation-vibration interactions. Further definitions for these terms are

$$\sigma = B_e(1 - \delta/2)\, hc/kT \ , \tag{55}$$

and

$$u = hc\omega/kT \ . \tag{56}$$

A procedure analogous to that of Mayer and Mayer[50] was used to expand the exponential and approximate the summation in equation (54). The contributions to the thermodynamic functions from internal degrees of freedom (designated by subscript i) then become

$$\begin{aligned} -\left(\frac{F_T^\circ - H_O^\circ}{RT}\right)_i &= \ln Q(v,j) = -\ln\sigma - \ln\psi + \sigma/3 + \sigma^2/90 + 2\rho/\sigma \\ &+ \delta e^{-u}/\psi + 2xue^{-2u}/\psi^2 \\ &+ 2x^2e^{-2u}u^2(1 + 4e^{-u})/\psi^4 + \delta^2e^{-u}/2\psi^2 \\ &+ 4\delta xue^{-2u}/\psi^3 - 6yue^{-3u}/\psi^3 + 2\phi e^{-2u}/\psi^2 \end{aligned} \tag{57}$$

$$\begin{aligned} \left(\frac{H_T^\circ - H_O^\circ}{RT}\right)_i &= 1 + ue^{-u}/\psi - \sigma/3 - \sigma^2/45 + 2\rho/\sigma + \delta e^{-u}u/\psi^2 \\ &+ 4xu^2e^{-2u}/\psi^3 - 2xue^{-2u}/\psi^2 + 6yue^{-3u}/\psi^3 \\ &- 18yu^2e^{-3u}/\psi^4 + 4x^2u^3e^{-2u}(1 + 7e^{-u} + 2e^{-2u})/\psi^5 \\ &- 4x^2u^2e^{-2u}(1 + 4e^{-u})/\psi^4 + 4\delta xu^2e^{-2u}(2 + e^{-u})/\psi^4 \ , \\ &- 4\delta xue^{-2u}/\psi^3 + \delta^2ue^{-u}(1 + e^{-u})/2\psi^3 + 4\phi e^{-2u}u/\psi^3 \ , \end{aligned} \tag{58}$$

and

$$\begin{aligned} \left(\frac{C_P^\circ}{R}\right)_i &= 1 + u^2e^{-u}/\psi^2 + 4\rho/\sigma + \sigma^2/45 + \delta e^{-u}u^2(1 + e^{-u})/\psi^3 \\ &- 8xu^2e^{-2u}/\psi^3 + 4xu^3e^{-2u}(2 + e^{-u})/\psi^4 \\ &+ 36yu^2e^{-3u}/\psi^4 - 18yu^3(3 + e^{-u})e^{-3u}/\psi^5 \end{aligned}$$

$$+ 4x^2u^2e^{-2u}(1 + 4e^{-u})/\psi^4 - 8x\delta u^2e^{-2u}(2 + e^{-u})/\psi^4$$

$$- 16x^2u^3e^{-2u}(1 + 7e^{-u} + 2e^{-2u})/\psi^5$$

$$+ \delta^2u^2e^{-u}(1 + 4e^{-u} + e^{-2u})/2\psi^4$$

$$+ 8x^2u^4e^{-2u}(1 + 12e^{-u} + 11e^{-2u} + e^{-3u})/\psi^6$$

$$+ 4\phi u^2e^{-2u}(2 + e^{-u})/\psi^4 + 4x\delta u^3e^{-2u}(4 + 7e^{-u} + e^{-2u})/\psi^5 \ , \qquad (59)$$

where

$$\psi = (1 - e^{-u}) \ . \qquad (60)$$

The total internal energy, ϵ_n , of the n^{th} electronic state is

$$\epsilon_n = E_e' + \omega v - \omega x v(v - 1) + \ldots , \qquad (61)$$

where E_e' is the electronic energy of the state expressed in wave numbers. Since, for a given electronic state, the energy of the lowest level ($v = 0$, $j = 0$) is taken as the reference point of the energy scale, E_e' becomes T_e (the electronic energy as defined by Herzberg[54]) less the difference between the zero point energies of the n^{th} state and the ground state; i. e.,

$$E_e' = T_e - \left[(1/2)\omega_e - (1/4)\omega_e x_e + (1/8)\omega_e y_e + \ldots\right]$$
$$+ \left[(1/2)\omega_e' - (1/4)\omega_e x_e' + (1/8)\omega_e y_e' + \ldots\right] , \qquad (62)$$

where the unprimed terms are for the ground state, and the primed terms are for the upper state.

The total internal partition function for all electronic states is given by

$$Q = \sum_n g_n (2j + 1)\, e^{-hc\epsilon_n/kT} = \sum_n g_n e^{-E_e/kT} \left\{ \sum_{v,j} (2j + 1)\exp\left[-uv + uxv(v - 1) + \ldots\right] \right\}$$

$$= \sum_n g_n e^{-E_e/kT} Q_n = \sum_n \frac{g_n e^{-E_e/kT}\, e^{\ln(Q_c)_n}}{\sigma\psi} , \qquad (63)$$

[54] Herzberg, G., Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules, Van Nostrand, N.Y. (1950).

where g_n is the multiplicity of the n^{th} electronic state, E_e is hcE'_e , Q_n and $(Q_c)_n$ are $Q(v,j)$ and Q_c , respectively, from equation (54).

The temperature derivatives of Q are therefore

$$\frac{dQ}{dT} = \sum_n g_n Q_n e^{-E_e/kT}(E_e/kT^2) + \sum_n g_n e^{-E_e/kT}(dQ_n/dT) , \tag{64}$$

$$\frac{d^2Q}{dT^2} = \sum_n g_n e^{-E_e/kT}(d^2Q_n/dT^2) + 2\sum_n g_n e^{-E_e/kT}(dQ_n/dT)(E_e/kT^2)$$

$$+ \sum_n g_n e^{-E_e/kT} Q_n (E_e/kT^2)^2 - 2\sum_n g_n e^{-E_e/kT} Q_n (E_e/kT^3) . \tag{65}$$

Values for Q_n and its derivatives are obtained from equations (66), (67), and (68).

$$Q_n = \frac{e^{\ln (Q_c)_n}}{\sigma\psi} , \tag{66}$$

$$dQ_n/dT = \frac{Q_n}{T}\left(\frac{H^\circ_T - H^\circ_0}{RT}\right)_{i,n} , \tag{67}$$

and

$$d^2Q_n/dT^2 = \frac{Q_n}{T^2}\left(\frac{C^\circ_p}{R}\right)_{i,n} + \frac{Q_n}{T^2}\left(\frac{H^\circ_T - H^\circ_0}{RT}\right)^2_{i,n} - \frac{2}{T}(dQ_n/dT) , \tag{68}$$

where

$$\ln(Q_c)_n = \sigma/3 + \sigma^2/90 + 2\rho/\sigma + \delta e^{-u}/\psi + \dots . \tag{69}$$

From the above expressions, the contribution of the internal energies of all electronic states to the thermodynamic functions (designated by the subscript Σi) may be derived.

$$-\left(\frac{F_T^\circ - H_0^\circ}{RT}\right)_{\Sigma i} = \ln Q \,, \tag{70}$$

$$\left(\frac{H_T^\circ - H_0^\circ}{RT}\right)_{\Sigma i} = (T/Q)(dQ/dT) \,, \tag{71}$$

$$\left(\frac{C_p^\circ}{R}\right)_{\Sigma i} = (2T/Q)(dQ/dT) - (T/Q)^2(dQ/dT)^2 + (T^2/Q)(d^2Q/dT^2)$$

$$= 2\left(\frac{H_T^\circ - H_0^\circ}{RT}\right)_{\Sigma i} - \left(\frac{H_T^\circ - H_0^\circ}{RT}\right)^2_{\Sigma i} + (T^2/Q)(d^2Q/dT^2) \,, \tag{72}$$

and

$$\left(\frac{S_T^\circ}{R}\right)_{\Sigma i} = \left(\frac{H_T^\circ - H_0^\circ}{RT}\right)_{\Sigma i} - \left(\frac{F_T^\circ - H_0^\circ}{RT}\right)_{\Sigma i} \,. \tag{73}$$

After addition of the contribution of translational degrees of freedom, changing of the reference temperature from 0° to 298.15°K, and substitution of the values of the fundamental constants adopted here, the total thermodynamic functions (in units of cal, °K, and moles) become

$$C_p^\circ = 1.98726\left(\frac{C_p^\circ}{R}\right)_{\Sigma i} + 4.96815 \,, \tag{74}$$

$$S_T^\circ = 1.98726\left(\frac{S_T^\circ}{R}\right)_{\Sigma i} + 6.8637533\log M + 11.4395881\log T$$

$$- 4.5758335\log\theta - 2.31538 \,, \tag{75}$$

$$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right) = -1.98726\left(\frac{F_T^\circ - H_0^\circ}{RT}\right)_{\Sigma i} + \frac{\left(H_{298}^\circ - H_0^\circ\right)_{\Sigma i}}{T}$$

$$+ 6.863753 \log M + 11.439588 \log T$$

$$- 4.575835 \log \theta + \frac{1481.2539}{T} - 7.28353 \, , \tag{76}$$

$$(H_T^\circ - H_{298}^\circ) = 1.98726T\left(\frac{H_T^\circ - H_0^\circ}{RT}\right)_{\Sigma i} - \left(H_{298}^\circ - H_0^\circ\right)_{\Sigma i}$$
$$+ 4.96815\,(T - 298.15) \, , \tag{77}$$

and

$$(H_{298}^\circ - H_0^\circ) = 592.5016\left(\frac{H_T^\circ - H_0^\circ}{RT}\right)_{\Sigma i, 298} + 1481.25392 \, , \tag{78}$$

where $\underline{M}$ is the molecular weight of the diatomic gas, and θ is the symmetry number of the molecule (1 for a heteronuclear and 2 for a homonuclear diatomic molecule).

The program for machine computation of the thermodynamic functions of diatomic gases was based on the above formulas. Calculations for the natural isotopic mixture of molecular oxygen are in excellent agreement with those of Woolley[55] when the spectroscopic constants he selected are used for the $^3\Sigma_g^-$, $^1\Delta_g$, $^1\Sigma_g^+$, $^3\Sigma_u^+$, and $^3\Sigma_u^-$ states. The results after minor adjustments are compared in Table IV.

Woolley's values were corrected for a change in the gas constant $\underline{R}$ and the Sackur-Tetrode constant and converted to a reference temperature of 298.15°K. Woolley used a different summation procedure and included some higher-order spectroscopic constants for the ground state which the present calculation does not include. He also broke off rotational sums at the dissociation limit, whereas they are extended here to infinite energy. The additional contribution to the enthalpy would be about 15 cal/gfw at 5000°K and negligible at 4000°K had he extended his rotational summation to infinite energy.

[55] Woolley, H.W., J. Research Nat. Bur. Stds. 40, 163 (1948); Nat. Bur. Stds. (U.S.) Circ. 564 (1955).

TABLE IV

COMPARISON OF THERMODYNAMIC FUNCTIONS OF MOLECULAR OXYGEN

Temp °K	S°_T cal/°K gfw		$-(F^\circ_T - H^\circ_{298})/T$ cal/°K gfw		$(H^\circ_T - H^\circ_{298})$ Kcal/gfw	
	Woolley[55]	Present Work	Woolley[55]	Present Work	Woolley[55]	Present Work
300	49.055	49.058	49.012	49.015	0.013	0.013
1000	58.199	58.200	52.773	52.774	5.427	5.427
2000	64.218	64.218	57.144	57.145	14.148	14.147
3000	67.980	67.980	60.165	60.166	23.447	23.441
4000	70 785	70.782	62.484	62.485	33.202	33.188
5000	73.028	73.028	64.376	64.379	43.259	43.249

F. POLYATOMIC MOLECULE CALCULATIONS

The program for the calculation of thermodynamic functions for ideal gases of polyatomic molecules was based upon the standard relations of molecular dynamics employed by spectroscopists.

One of these basic relations is that the total energy of an ideal polyatomic molecule is the sum of its translational and internal energies.

$$\epsilon = \epsilon_t + \epsilon_{int} \; . \tag{79}$$

The internal energy is composed of electronic, vibrational, rotational, and interaction or coupling contributions. The interaction terms are rarely, if ever, accurately known and are usually ignored. The internal energy was therefore considered to be the sum of the electronic, vibrational, and rotational contributions.

$$\epsilon_{int} = \epsilon_r + \epsilon_v + \epsilon_{el} \; . \tag{80}$$

The partition function (Q) can then be written as the product of the individual partition functions

$$Q = Q_t Q_r Q_v Q_{el} \; , \tag{81}$$

and the thermodynamic functions can be separated into sums of translational, rotational, vibrational, and electronic contributions.

$$C_p^\circ = C_{p(t)}^\circ + C_{p(r)}^\circ + C_{p(v)}^\circ + C_{p(el)}^\circ \; , \tag{82}$$

$$H_T^\circ - H_0^\circ = \left(H_T^\circ - H_0^\circ\right)_t + \left(H_T^\circ - H_0^\circ\right)_r + \left(H_T^\circ - H_0^\circ\right)_v + \left(H_T^\circ - H_0^\circ\right)_{el} \; , \tag{82A}$$

$$-\left(\frac{F_T^\circ - H_0^\circ}{T}\right) = -\left(\frac{F_T^\circ - H_0^\circ}{T}\right)_t - \left(\frac{F_T^\circ - H_0^\circ}{T}\right)_r - \left(\frac{F_T^\circ - H_0^\circ}{T}\right)_v - \left(\frac{F_T^\circ - H_0^\circ}{T}\right)_{el} \; , \tag{82B}$$

and

$$S_T^\circ = S_t^\circ + S_r^\circ + S_v^\circ + S_{el}^\circ \; . \tag{82C}$$

Evaluation of the Q's in the usual manner,[50] combination of the translational and rotational contributions, and substitution of required physical constants[1] then leads to the following equations which were employed in the computer program:

1. Linear Polyatomic Molecules

a. Heat Capacity in cal/° K mole

$$C_p^\circ = C_{p(t,r)}^\circ + C_{p(v)}^\circ + C_{p(el)}^\circ \quad , \tag{83}$$

$$C_{p(t,r)}^\circ = 6.95541 + 0.091420 \left(\frac{B}{T}\right)^2 \quad , \tag{84}$$

$$B = 2.79889 \times 10^{-39}/I \quad , \tag{85}$$

$$C_{p(v)}^\circ = \sum_i \frac{1.98726 \left(\frac{1.43880\,\omega_i}{T}\right)^2 \left(e^{-\frac{1.43880\,\omega_i}{T}}\right)}{\left(1 - e^{-\frac{1.43880\,\omega_i}{T}}\right)^2} , \tag{86}$$

$$C_{p(el)}^\circ = \frac{4.113917}{T^2} \left[\frac{Q_2}{Q} - \left(\frac{Q_1}{Q}\right)^2\right] , \tag{87}$$

$$Q = \sum_i g_i \, e^{-\frac{1.43880\,\epsilon_i}{T}} \quad , \tag{88}$$

$$Q_1 = \sum_i \epsilon_i \, g_i \, e^{-\frac{1.43880\,\epsilon_i}{T}} \quad , \tag{89}$$

$$Q_2 = \sum_i \epsilon_i^2 \, g_i \, e^{-\frac{1.43880\,\epsilon_i}{T}} \quad , \tag{90}$$

ω_i is a fundamental frequency in units of cm^{-1}, I is the principal moment of inertia, ϵ_i is an electronic energy level in units of cm^{-1}, and g_i is the degeneracy of the corresponding electronic energy level.

b. Enthalpy in cal/mole

$$H_T^\circ - H_{298}^\circ = \left(H_T^\circ - H_0^\circ\right)_{t,r} + \left(H_T^\circ - H_0^\circ\right)_v$$

$$+ \left(H_T^\circ - H_0^\circ\right)_{el} - \left(H_{298}^\circ - H_0^\circ\right)_{t,r,v,el} \quad , \tag{91}$$

$$\left(H_T^\circ - H_0^\circ\right)_{t,r} = T\left[6.95541 - 0.953090\left(\frac{B}{T}\right) - 0.091420\left(\frac{B}{T}\right)^2\right] \quad , \tag{92}$$

$$\left(H_T^\circ - H_0^\circ\right)_v = \sum_i \frac{1.98726T\left(\frac{1.43880\omega_i}{T}\right)\left(e^{-\frac{1.43880\omega_i}{T}}\right)}{1 - e^{-\frac{1.43880\omega_i}{T}}} \quad , \tag{93}$$

$$\left(H_T^\circ - H_0^\circ\right)_{el} = 2.859270\left[\frac{Q_1}{Q}\right] \quad , \tag{94}$$

$$\left(H_{298}^\circ - H_0^\circ\right)_{t,r,v,el} = 298.15\left[6.95541 - 0.953090\left(\frac{B}{298.15}\right) - 0.091420\left(\frac{B}{298.15}\right)^2\right]$$

$$+ \left[\sum_i 1.98726(298.15)\frac{\left(\frac{1.43880\omega_i}{298.15}\right)\left(e^{-\frac{1.43880\omega_i}{298.15}}\right)}{\left(1 - e^{-\frac{1.43880\omega_i}{298.15}}\right)}\right]$$

$$+ \left[2.859270 \cdot \frac{\sum_i \epsilon_i g_i e^{-\frac{1.43880\epsilon_i}{298.15}}}{\sum_i g_i e^{-\frac{1.43880\epsilon_i}{298.15}}}\right] \tag{95}$$

c. Free-Energy Function in cal/° K mole

$$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right) = -\left(\frac{F_T^\circ - H_0^\circ}{T}\right)_{t,r} - \left(\frac{F_T^\circ - H_0^\circ}{T}\right)_v - \left(\frac{F_T^\circ - H_0^\circ}{T}\right)_{el} + \left(\frac{H_{298}^\circ - H_0^\circ}{T}\right)_{t,r,v,el} \tag{96}$$

$$-\left(\frac{F_T^\circ - H_0^\circ}{T}\right)_{t,r} = 6.863753 \log M + 11.439588 \log T - 4.575835 \log\left(\frac{B\theta}{T}\right) + 0.953090\left(\frac{B}{T}\right) + 0.045710\left(\frac{B}{T}\right)^2 - 8.00651 \ , \tag{97}$$

$$-\left(\frac{F_T^\circ - H_0^\circ}{T}\right)_v = -\sum_i 4.575835 \log\left(1 - e^{-\frac{1.43880\omega_i}{T}}\right) \ , \tag{98}$$

$$-\left(\frac{F_T^\circ - H_0^\circ}{T}\right)_{el} = 4.575835 \log \sum_i g_i \, e^{-\frac{1.43880\epsilon_i}{T}} \ . \tag{99}$$

B, ω_i and ϵ_i were defined earlier. M is the molecular weight, and θ is the symmetry number.

d. Entropy in cal/° K mole

$$S_T^\circ = \left(\frac{H_T^\circ - H_{298}^\circ}{T}\right) - \left(\frac{F_T^\circ - H_{298}^\circ}{T}\right) \ . \tag{100}$$

2. Nonlinear Polyatomic Molecules

a. Heat Capacity in cal/° K mole

Equations (83), (86), and (87) through (90) were used with

$$C^\circ_{p(t,r)} = 7.949040 \tag{101}$$

b. Enthalpy in cal/mole

$$H^\circ_T - H^\circ_{298} = \left(H^\circ_T - H^\circ_0\right)_{t,r} + \left(H^\circ_T - H^\circ_0\right)_v + \left(H^\circ_T - H^\circ_0\right)_{el} - \left(H^\circ_{298} - H^\circ_0\right)_{t,r,v,el} \quad , \tag{102}$$

$$\left(H^\circ_T - H^\circ_0\right)_{t,r} = 7.949040\, T \quad , \tag{103}$$

$$\left(H^\circ_{298} - H^\circ_0\right)_{t,r,v,el} = \left[7.949040(298.15)\right]$$

$$+ \left[\sum_i \frac{1.98726(298.15)\left(\frac{1.43880\omega_i}{298.15}\right)\left(e^{-\frac{1.43880\omega_i}{298.15}}\right)}{1 - e^{-\frac{1.43880\omega_i}{298.15}}}\right]$$

$$+ \left[2.859270 \frac{\sum_i \epsilon_i g_i e^{-\frac{1.43880\epsilon_i}{298.15}}}{\sum_i g_i e^{-\frac{1.43880\epsilon_i}{298.15}}}\right] \quad . \tag{104}$$

$(H_T^\circ - H_0^\circ)_v$ and $(H_T^\circ - H_0^\circ)_{el}$ are given by equations (93) and (94). All other parameters are as previously defined.

c. Free-Energy Function in cal/° K mole

$$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right) = -\left(\frac{F_T^\circ - H_0^\circ}{T}\right)_{t,r} - \left(\frac{F_T^\circ - H_0^\circ}{T}\right)_v$$

$$-\left(\frac{F_T^\circ - H_0^\circ}{T}\right)_{el} + \left(\frac{H_{298}^\circ - H_0^\circ}{T}\right)_{t,r,v,el} \qquad (105)$$

$$\begin{aligned}-\left(\frac{F_T^\circ - H_0^\circ}{T}\right)_{t,r} &= 6.863753 \log M + 18.303341 \log T \\ &- 4.575835 \log \theta + 2.287918 \log I_A I_B I_C \times 10^{120} \\ &- 17.16242. \qquad (106)\end{aligned}$$

$-\left(\frac{F_T^\circ - H_0^\circ}{T}\right)_v$ and $-\left(\frac{F_T^\circ - H_0^\circ}{T}\right)_{el}$ are given by equations (98) and (99).

$I_A I_B I_C$ is the product of the three principal moments of inertia. All other parameters are as previously defined.

d. Entropy in cal/ °K mol (given by Eq. 100).

G. CONDENSED-PHASE CALCULATIONS

Solid and liquid-phase thermodynamic functions are calculated in essentially the same way. Calculations for both phases can therefore be discussed together.

1. Solid Phases

a. Basic Equations

In a reference state table, only C_p°, S_T°, $-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)$, and $(H_T^\circ - H_{298}^\circ)$ are included. For the solid phase, the last three functions can be calculated if C_p° and solid-state transition data are available. The formulas for a solid with n first order transitions below the temperature T and above the reference temperature are

$$S_T^\circ = \int_0^{T_1} \left(\frac{C_p^\circ}{T}\right) dT + \sum_{i=1}^{n} \lambda_i/T_i + \sum_{i=2}^{n} \int_{T_{i-1}}^{T_i} \left(\frac{C_p^\circ}{T}\right) dT + \int_{T_n}^{T} \left(\frac{C_p^\circ}{T}\right) dT \tag{107}$$

$$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right) = S_T^\circ - \left(\frac{H_T^\circ - H_{298}^\circ}{T}\right), \tag{108}$$

$$H_T^\circ - H_{298}^\circ = \int_{298.15}^{T_1} C_p^\circ dT + \sum_{i=1}^{n} \lambda_i + \sum_{i=2}^{n} \int_{T_{i-1}}^{T_i} C_p^\circ dT + \int_{T_n}^{T} C_p^\circ dT, \tag{109}$$

$$H_T^\circ - H_{298}^\circ = (H_T^\circ - H_0^\circ) - (H_{298}^\circ - H_0^\circ), \tag{110}$$

where λ_i is the heat of the i^{th} transition at T_i. The solid-liquid transition can be included as the n^{th} one in which case, the C_p° of the liquid is used in the last term of eqs. (107) and (109).

b. Method of Choosing Basic Data

Since experimental C_p° data are often reported directly in the literature and since empirical equations are often presented for the temperature dependence of this quantity, there appear to be several advantages for conducting calculations with this quantity, rather than doing so with other quantities such as $(H_T^\circ - H_{298}^\circ)$. Therefore, in the work of this project, first priority was given to locating C_p° data for each solid as it came under consideration. The second step was to plot graphs and compare the data from various sources. After a choice of the "best" data was made, several alternatives presented themselves for proceeding with the calculations, depending upon the state of the available C_p° data.

1) The "best" data for C_p° and the other functions may already have been tabulated at the desired temperatures throughout the entire temperature range of the tables.

2) Data may have been tabulated only for portions of the desired temperature range.

3) The C_p° data may have been in the form of data points given at various temperature intervals.

4) The C_p° data may have been presented in the form of an analytical expression. A variety of possible analytical expressions have been used. These include Debye or Einstein functions, polynominals, etc.

c. Machine Computation

The computer program used on this project for condensed phases was designed to accept numerical values of C_p° at the 100°K intervals required in the final tables and carry out a numerical integration of these input data to give the other thermodynamic quantities. This eliminated the need for first reducing the original data to an analytical expression.

d. Uncertainty Analysis

The standard procedure adopted in the computation of error estimates has been to assign uncertainties to the primary C_p° and heat-of-transition data and to calculate the uncertainties in the derived functions S_T°, $-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)$, and $(H_T^\circ - H_{298}^\circ)$ from them. An assigned uncertainty could be made at each of the tabular temperatures. Since highly precise calculations were not expected in these cases, an average value for the uncertainty in a given temperature interval was used.

1) Heat capacity

Heat capacities are usually obtained experimentally, and the original experimenter is the one best able to set the uncertainty limits. However, this is often neglected and must be done instead by the reviewer. If data from several sources are available, the spread in the data can give some indication of their reliability. Questions of purity of samples, the method of, and the care taken in the measurements, etc., should all be considered.

2) Entropy

The range of heat capacity values is defined as

$$C_p^\circ = C_{po}^\circ \pm \delta C_p^\circ \quad , \tag{111}$$

where

$$\delta C_p^\circ = (C_{pU}^\circ - C_{pL}^\circ)/2 \quad , \tag{112}$$

C_{po}° = best value for heat capacity available,

C_{pU}° = upper limit of uncertainty range,

and

C_{pL}° = lower limit of uncertainty range.

The true value C_{pt}° is expected to lie somewhere between the limits given by equation (111).

From the thermodynamic definition of entropy, one can write

$$S_T^\circ = S_{298,o}^\circ \pm s_{298} + \int_{298}^{T} \frac{C_{po}^\circ}{T}\, dT \pm \int_{298}^{T} (\delta C_p^\circ/T)\, dT \ , \tag{113}$$

where

$S_{298,o}^\circ$ = the best available value of S_{298}°, and

s_{298} = the uncertainty in S_{298}°.

The uncertainty in S°_T is therefore,

$$s_T = s_{298} + \int_{298}^{T} (\delta C^\circ_p/T)\,dT. \tag{114}$$

Or assuming that $\delta C^\circ_p \neq f(T)$,

$$s_T = s_{298} + \delta C^\circ_p \ \ln (T/298.15) \tag{115}$$

is obtained.

3) Enthalpy

Since

$$H^\circ_T - H^\circ_{298} = \int_{298.15}^{T} C^\circ_p\,dT, \tag{116}$$

one obtains, for an actual point with its associated uncertainties,

$$H^\circ_T - H^\circ_{298} + \delta(H^\circ_T - H^\circ_{298}) = \int_{298.15}^{T} C^\circ_{po}\,dT + \int_{298.15}^{T} \delta C^\circ_p\,dT \tag{117}$$

from equation (111). The uncertainty in $H^\circ_T - H^\circ_{298}$ is therefore,

$$h_T = \int_{298.15}^{T} \delta C^\circ_p\,dT = \delta(H^\circ_T - H^\circ_{298}) \tag{118}$$

4) Free energy Function

The uncertainty in the free-energy function defined as

$$f_T = \delta\left(\frac{F^\circ_T - H^\circ_{298}}{T}\right) \tag{119}$$

can be obtained from those of the entropy and enthalpy functions just discussed because of equation (100). Due to this equation, one can simply write the uncertainty in the free-energy function as

$$f_T = s_T - h_T/T \ . \tag{120}$$

This is contrary to the usual practice in summing errors because in this particular case, the uncertainties s_T and h_T are due to a common uncertainty in C°_p and are matched. The independent error in S°_{298} is simply added on.

From equations (114) and (118), it can be seen that $s_T > h_T/T$.

2. Liquid Phases

The calculation of thermodynamic functions for liquid phases was done in essentially the same manner as described above for solid phases. Primary heat capacity data were scantier and less precise for liquid phases and more ingenuity in making estimates was required.

H. EVALUATION OF STANDARD HEAT OF FORMATION OF ELEMENTS AT 298.15°K$[\Delta H^\circ_{f298}]$

Heats of vaporization or sublimation may be derived from vapor pressure measurements in two different ways.

The first technique, based on the Clausius-Clapeyron equation, is called the "Second Law Method." When applied to the vaporization of an element it will give a single value of ΔH°_{f298} equal to ΔH°_{v298} or ΔH°_{s298} from each set of vapor pressure measurements.

If it is assumed that the vapor of the element is ideal, the Clausius-Clapeyron equation may be written as a form of Van't Hoff's equation,

$$\frac{d(-R\ln K_p)}{dT} = -\frac{\Delta H^\circ_f}{T^2} \quad , \tag{121}$$

where K_p is the equilibrium constant for the vaporization process. For the special case of liquid or solid vaporization without polymerization, K_p equals the vapor pressure.

The heat of formation, ΔH°_f, may be obtained as a function of the temperature from the equation

$$\Delta H^\circ_f = \Delta H^\circ_{f298} + \int_{298}^{T} \Delta C^\circ_p \, dT \quad , \tag{122}$$

where ΔC°_p is the difference between the heat capacity of the gas and that of the condensed phase. The exact analytical expression used for ΔC°_p will depend on the precision of available heat capacity data and on the form of the functions used to express the temperature dependence of the heat capacities of both phases concerned. If the form of the expression for ΔC°_p is that favored by Kelley[56] for the heat capacity of solids; namely,

$$\Delta C^\circ_p = \Delta A + \Delta BT - \Delta CT^{-2} \tag{123}$$

where the coefficients are related to those of the enthalpy expression by $\Delta A = \Delta a$ $\Delta B = 2\Delta b$ and $\Delta C = \Delta c$, equation (122) then becomes

$$\Delta H^\circ_f = (\Delta H^\circ_{f298} + \Delta A(T - 298.15) + \frac{\Delta B}{2}[T^2 - (298.15)^2] + \Delta C(1/T - 1/298.15). \tag{124}$$

[56]Kelley, K. K., Bureau of Mines Bull. 584 (1960).

If equation (124) is substituted into equation (121), the result may be integrated and re-arranged to give

$$- R \ln K + \Delta A \ln T + \frac{\Delta BT}{2} - \frac{\Delta CT^{-2}}{2} + \Delta DT^{-1} = \frac{\Delta H^{\circ}_{f298}}{T} + I \ , \qquad (125)$$

where

$$\Delta D = 298.15 \Delta A + \frac{(298.15)^2 \Delta B}{2} + \frac{\Delta C}{298.15} \ , \qquad (126)$$

and I is an integration constant. If terms on the left-hand side of equation (125) are designated by Σ, the equation becomes

$$\sum = \frac{\Delta H^{\circ}_{f298}}{T} + I \ . \qquad (127)$$

Therefore, one may calculate ΔH°_{f298}, by the Second Law Method, by computing Σ for each experimental vapor pressure measurement, and plotting it against the reciprocal of the temperature. The resulting plot should be a straight line, and the slope of that line is the value of ΔH°_{f298}. The constant of integration, I, is related to the entropy of formation at 298.15° K by the equation

$$\Delta S^{\circ}_{f298} = \Delta A + \Delta A \ln (298.15) + \Delta B (298.15) + \frac{\Delta C (298.15)^{-2}}{2} - I \qquad (128)$$

When free-energy functions are available for the condensed and gas phases, these functions may be used in combination with experimental vapor pressure data to calculate a value of ΔH°_{f298} for each vapor pressure measurement. This technique is known as the "Third Law Method." Thus, the difference between the free-energy functions of the gas and condensed phases, Δ(f.e.f.) is

$$\Delta(\text{f.e.f.}) = \left[\frac{F^{\circ}_T - H^{\circ}_{298}}{T}\right]_g - \left[\frac{F^{\circ}_T - H^{\circ}_{298}}{T}\right]_c = \frac{\Delta F^{\circ}_f}{T} - \frac{\Delta H^{\circ}_{f298}}{T} \ . \qquad (129)$$

However,

$$\frac{\Delta F_f^\circ}{T} = -R \ln K_p . \qquad (130)$$

Therefore,

$$\Delta H^\circ_{f298} = T\,[-R \ln K_p - \Delta(f.e.f.)] \qquad (131)$$

Ideally, the two methods should give the same results. In practice, they seldom do because of errors in the experimental results or approximations made in analytical expressions for the temperature dependence of heat capacities in the Second Law treatment. The Third Law treatment is to be preferred for the present work, and was the one adopted. Because the latter method permits a calculation of ΔH_f° corresponding to each vapor pressure measurement, a sensitive check for a possible drift with temperature is available. Calculations are possible for situations in which the temperature dependence of heat capacities may not have been reduced to an analytical expression. Most important however, the thermodynamic compilations are thereby made internally consistent. In this way, experimental vapor pressures are more closely reproduced from the compilations than they would be if the Second Law treatment were used. In that sense, the values of ΔH°_{f298} listed will be legitimately used only with the free-energy functions for gas and condensed phases with which they are tabulated.

The two techniques just described have general applicability to the vaporization of systems other than those of the elements. When applied to the vaporization of compounds, however, they simply yield heats of the vaporization or decomposition process which yields the vapor species.

IV. REVIEWS OF DATA AND COMPUTATION SUMMARIES FOR INDIVIDUAL ELEMENTS AND COMPOUNDS

With the exception of Th and Ce for which there were insufficient data, ideal monatomic gas tables were prepared for all the elements within the scope of the contract plus several other metals which were included at the request of Materials Central, WADD. Emphasis was placed initially on the preparation of tables for the elements because they were needed for the preparation of tables on compounds. In some cases, it was only necessary to add uncertainty estimates to existing tables for the elements. A number of existing tables were re-computed because better energy level data had become available. Oxide compounds were also given high priority in the work because more data were available on them than on the other classes of compounds such as the carbides, borides, and nitrides.

A. ELEMENTS

1. Beryllium

a. Crystal Structure and Melting Point

At room temperature, elemental beryllium has a hexagonal, close-packed structure.[57] The possible allotropy of beryllium has been a subject of dispute for over thirty years. In general, two allotropic transformations have been discussed; one occurring in the temperature range from 400° to 800°C, and the other around 20° to 30°C below the melting point. Most of the evidence in support of allotropy in the lower-temperature range can probably be discounted as originating from impure beryllium. The most likely impurity, BeO, will not be revealed by the usual spectroscopic analysis.

Lewis[58] inferred the existence of allotropic transformations at -45 and 450°C by thermal emf and electrical resistivity measurements. Jaeger and Rosenbohm[59] found evidence for a second beryllium phase from specific heat measurements. From X-ray measurements, Jaeger and Zanstra[60] proposed that, β-Be is hexagonal close-packed with a relatively large unit cell and is metastable at room temperature. They also reported that the high-temperature phase was most successfully produced by heating to 630°C. Kosolapov and Trapoznikov[61] obtained

[57] Pearson, W.B., Handbook of Lattice Spacings and Structures of Metals, Pergamon Press, N.Y. (1958).

[58] Lewis, E.J., Phys. Rev. 34, 1575 (1929).

[59] Jaeger, F.M. and E. Rosenbohm, Proc. Acad. Sci. (Amsterdam) 35, 1055 (1932); Proc. Acad. Sci. (Amsterdam) 37, 67 (1934); Rec. trav. chim. 53, 451 (1934).

[60] Jaeger, F.M. and J.E. Zanstra, Proc. Acad. Sci. (Amsterdam) 36, 636 (1933).

[61] Kosolapov, G.F. and A.K. Trapoznikov, J. Exper. Theor. Phys. (U.S.S.R.) 6, 1136 (1936).

evidence for allotropy from extra reflections in X-ray measurements on beryllium samples. Noyce and Daane[62] reported an allotropic transformation at 730°C from thermal and dilatometric effects. However, Gordon and Kaufmann[63] were unable to confirm the latter results. Gordon[64] measured the thermal coefficients of expansion of beryllium up to 1000°C by X-ray methods, and found no evidence for allotropy. However, Chatterjee and Sidhu[65] reported allotropy by X-ray measurements on 99.9 percent pure beryllium. Sidhu and Henry[66] examined spectroscopically pure beryllium and very dilute gold-beryllium alloys, and from the position and intensity variations of extra lines, concluded that a β-Be phase was present which had a complex hexagonal structure. Seybolt et al[67] criticized these conclusions and stated that the extra reflections were probably due to BeO or $AuBe_5$. Kaufmann et al[68] found no evidence for allotropy by thermal analysis studies and microstructure examination of beryllium that had been cooled down from temperatures up to the melting point. The last investigators further stated that the fact that single crystals of beryllium could be successfully grown from the melt was evidence for the nonexistence of the disputed phase.

In addition to the questionable allotropic transformation below 1000°C, a double thermal arrest has been reported in the temperature range from 1250° to 1260°C (20 or 30 degrees below the melting point).[69-72] This observation has been variously interpreted as due to an allotropic transformation or the presence of a eutectic with a contaminant. Losano[73] reported finding only a single thermal arrest in 99.96 percent pure beryllium. However, Martin and Moore[74] later found no evidence, with thermal analysis techniques, for the existence of a solid-state change between 25° and 1000°C, but they detected a double thermal arrest in the vicinity of the melting point. On cooling, the second arrest started on the average 20°C below the melting point arrest; on heating, the average was 17°C below the melting point. The latter measurements

[62] Noyce, W.K. and A.H. Daane, AEC Rept. No. CT-2404 (15 March 1945).

[63] Gordon, P. and A.R. Kaufmann, AEC Rept. No. CT-3379 (11 December 1945).

[64] Gordon, P., J. Appl. Phys. 20, 908 (1949).

[65] Chatterjee, G.P. and S.S. Sidhu, Phys. Rev. 76, 175 (1949).

[66] Sidhu, S.S. and C.O. Henry, J. Appl. Phys. 21, 1036 (1950).

[67] Seybolt, A., J.S. Lukesh, and D.W. White, J. Appl. Phys. 22, 986 (1951).

[68] Kaufmann, A.R., P. Gordon, and D.W. Lillie, Trans. ASM 42, 785 (1950).

[69] Sloman, H., J. Inst. Metals, 50, 365 (1932).

[70] Teitel, R.J. and M. Cohen, J. Metals 185, 285 (1949).

[71] Tuer, G.L., Fundamental Mechanical and Physical Characteristics of Beryllium As Related to Single Crystals, Sc.D. Thesis, M.I.T. (1954).

[72] Buzzard, R.W., J. Research Nat. Bur. Stds. 50, 63 (1953).

[73] Losano, L., Alluminio 8, 67 (1939).

[74] Martin, A. and A. Moore, J. Less Common Metals, 1, 85 (1959).

were made on beryllium samples of varying purity and included zone-refined beryllium containing 0.056 weight percent of metallic impurities, 0.4 cc/g of H_2, and 0.008 weight percent of O_2. They also reported lattice spacings for 99.4 percent pure beryllium containing 0.3 weight percent of BeO from -193° to 1265°C. They found deviations from linearity for the temperature dependence of the lattice spacings at about 200° and 800°C. These deviations were attributed to the effects of solutes. A discontinuity in lattice spacings at about 1250°C was stated to coincide with the transformation of hexagonal close-packed β-beryllium to body-centered cubic α-beryllium.

It was concluded, in summary, that beryllium is hexagonal, close-packed from room temperature to about 20 degrees below its melting point. A transformation to a body-centered cubic phase is quite possible at the latter temperature, but was ignored in the present compilation.

The melting point of beryllium was taken as 1556° ±3°K on the basis of the available information.[56, 75-78]

b. Thermodynamic Properties

1) Heat of fusion

The heat of fusion of beryllium was taken as 2.800 ± 0.500 Kcal/gfw from the review of Kubaschewski et al.[79] This value was derived from Oesterheld's[80] thermal analysis studies (2.40 Kcal/gfw), Losano's[73] measurements on the pressure dependence of the melting point (1.98, 2.23, 2.56 Kcal/gfw), Sloman's[81] measurements on the melting-point depression of beryllium by silver (3.4 Kcal/gfw), and regularities among the entropies of transformation of the alkali and alkaline earth metals (3.0 Kcal/gfw). It should be noted that the value for the heat of fusion of magnesium accepted here destroys some of the regularity of Kubaschewski's comparison. However, the limits of error assigned to the value are probably adequate to cover any shift in the estimated value. The heat of fusion of beryllium adopted here was the one in general acceptance.[56, 75-78]

[75]Dergazarian, T.E. et.al. JANAF Interim Thermochemical Tables, vols 1 and 2, Dow Chem. Co. (31 December 1960).

[76]Hultgren, R. et.al. Selected Values for the Thermodynamic Properties of Metals and Alloys, Min. Res. Lab., Inst. of Eng. Res., Univ. of California, Berkeley (1956); rev. eds. (1958 and (1960).

[77]Stull, D.R. and G.C. Sinke, Thermodynamic Properties of the Elements, No. 18, In: Advances in Chemistry Series, Am. Chem. Soc., Washington (1956).

[78]National Bureau of Standards Rept 6484 (1959).

[79]Kubaschewski, O., P. Brizgys, O. Huchler, R. Jauch, and K. Reinartz, Z. Elektrochem. 54, 275 (1950).

[80]Oesterheld, G., Z. Anorg. u. allgem. Chem. 97, 1 (1916).

[81]Sloman, H.A., J. Inst. Metals 54, 161 (1934).

2) <u>Entropy and heat content at 298.15°K</u>

Values of the entropy and heat content of elemental beryllium at 298.15°K were based on the measurements of Hill and Smith[82] (4° to 300°K). These data have been joined with the high-temperature data of Ginnings, Douglas, and Ball[83] (367° to 1169°K) by the Bureau of Standards.[78] S°_{298} was calculated to be 2.282 ± 0.02 e.u., and $(H^\circ_{298} - H^\circ_0)$ was computed to be 467 cal/gfw by the Bureau of Standards. The latter values were accepted for the present work. These same low-temperature data have been used elsewhere[75, 76] to calculate the value of S°_{298} = 2.280 e.u.

Other low-temperature heat capacity measurements on beryllium included those of Simon and Ruhemann[84] (71° to 79°K), Lewis[58] (97° to 463°K), and Cristescu and Simon[85] (10° to 300°K).

3) <u>High-temperature heat content</u>

The measurements of Ginnings, Douglas, and Ball[83] (367° to 1169°K) were used to calculate the high-temperature heat capacity and heat content of beryllium. These authors gave results for two samples, each of which contained 99.5 percent beryllium, but differed in the composition of their impurities. An average of the results for the two samples, which differed a maximum of 0.5 percent, was adopted. The heat contents to 1000°K were considered to be good to ± 1 percent. The uncertainty of an extrapolation from the highest temperature of measurement (1169°K) to the melting point is larger. Derived values of the heat capacity, which increase essentially at a uniform rate with temperature from 700° to 1000°K, show an inflection around 1000°K to a more rapid increase with temperature. The extrapolation made herein assumed that the heat capacity above 1100°K increases at the same rate as it does between 1000° and 1100°K; namely, 2.5×10^{-3} cal/$^{o}K^2$ gfw. Between 1000°K and the melting point, the heat capacities were considered to be good to ± 3 percent. It should be noted that the temperature of the observed inflection lies in the region of one of the disputed allotropic transformations discussed above.

[82] Hill, R.W. and P.L. Smith, Phil. Mag. <u>44</u>, 636 (1953).

[83] Ginnings, D.C., T.B. Douglas, and A.F. Ball, J. Am. Chem. Soc. <u>73</u>, 1236 (1951).

[84] Simon, F. and H. Ruhemann, Z. physik. Chem. <u>129</u>, 321 (1927).

[85] Cristescu, S. and F. Simon, Z. physik. Chem. <u>25B</u>, 273 (1934).

Other available data for the high-temperature heat capacity or heat content of solid beryllium included those of Fieldhouse et al[86] (434° to 1328°K), Jaeger and Rosenbohm[59] (273° to 1338°K), Lewis[58] (282° to 463°K), Magnus and Holzmann[87] (295° to 1173°K), and Nilson and Pettersson[88] (273° to 573°K).

In the absence of experimental data for the heat capacity of liquid beryllium, the value of 7.50 cal/°K gfw recommended by Kelley[56] was used.

4) Heat of formation of monatomic gas

The Third Law Method was used with the free-energy functions for beryllium tabulated herein and the vapor pressure data from the following sources to give the indicated values for the heat of formation of beryllium at 298.15°K:

Source	Temperature (°K)	ΔH_f° at 298.15°K (Kcal/gfw)
Gulbransen and Andrew[89]	1103 - 1229	78.170 ± 0.600
Holden et al[90]	1172 - 1552	77.840 ± 0.700
Schuman and Garrett[91]	1174 - 1336	80.590 ± 1.300
Baur and Brunner[92]	1850 - 2331	79.540 ± 2.500

Original data points were used for the calculations.

The value for ΔH°_{f298} adopted herein was an average of the results of the first two authors listed; namely, 78.00 ± 0.500 Kcal/gfw. The uncertainty given was based on the scatter of experimental vapor pressures, and did not include uncertainties due to estimated heat capacities for liquid beryllium.

[86] Fieldhouse, I.B., J.C. Hedge, J.I. Lang, and T.E. Waterman, Wright Air Development Center, Tech. Rept. WADC-TR-57-487, AD-1550954 (1958).

[87] Magnus, A. and H. Holzmann, Ann. Physik (5) 3, 585 (1929).

[88] Nilson, L.F. and O. Pettersson, Oversigt Kongl. Svenska Vetenskaps-Akad. 37, 33 (1880).

[89] Gulbransen, E.A. and K.F. Andrew, J. Electrochem. Soc. 97, 383 (1950).

[90] Holden, R.B., R. Speiser, and H.L. Johnston, J. Am. Chem. Soc. 70, 3897 (1948).

[91] Schuman, R. and A.B. Garrett, J. Am. Chem. Soc. 66, 442 (1944).

[92] Baur, E. and R. Brunner, Helv. Chim. Acta 17, 958 (1934).

An extrapolation of ΔF_f° to zero gave a normal boiling point for beryllium of 2754°K. An uncertainty of 50 degrees was estimated for the boiling point from uncertainties in ΔH°_{f298} and liquid heat capacities. At the boiling point, ΔH_f° was calculated to be 70.498 Kcal/gfw.

5) Thermodynamic functions

The beryllium reference state thermodynamic functions are given in Table V.

The thermodynamic functions for beryllium as an ideal monatomic gas in Table VI were calculated using all the levels listed by Moore.[52] $H^\circ_{298} - H^\circ_0$ was found to be 1,481 cal/mole. Uncertainity estimates are given on the backs of the tables.

2. Boron

Existing tabulations on boron were found to be inadequate for three reasons. First, they were not based upon the most up-to-date data; second, they did not extend up to 6000°K; and third, estimates of uncertainty in the data were not included. Therefore, the re-computation of the boron data was undertaken.

a. Crystal Structure

Elemental boron exists in several modifications. However, the stable modifications and their temperature ranges of stability are still in doubt.

It is generally accepted that β- rhombohedral boron is the stable form above 1500°C,[93-95] and also that it may be stable down to as low as 1100°C.[93] α-rhombohedral boron is also fairly well documented,[96, 97] being stable at lower temperatures than the β-rhombohedral form.[94] Other common forms include the tetragonal,[98, 99] and amorphous borons.[94] Several other polymorphs have been reported, but it appears likely that many of them are formed as a result of kinetic considerations and the presence of a foreign substrate and have no real thermodynamic range of stability.[93]

In view of the uncertainties regarding the stable phases of boron, it is impossible to specify solid transition-point temperatures. Such transitions usually have low but generally unknown heats of transition (commonly a few hundred calories). Hence, the thermodynamic tabulations will contain these added uncertainties.

b. Melting Point

For the melting point of boron, there were also many reported values. These are summarized in Table VII.

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[93]Hoard, J.L. and A. E. Newkirk, An analysis of polymorphism in boron based upon X-ray diffraction results, J. Am. Chem. Soc. 82, 70 (1960).

[94]Williams, D.N., The Properties of Boron, Defense Metals Information Center, Battelle Memorial Institute, Memorandum 41 (4 January 1960).

[95]Sands, D.E. and J.L. Hoard, Rhombohedral elemental boron, J. Am. Chem. Soc. 79, 5582 (1957).

[96]Decker, B.F. and J.S. Kasper, The crystal structure of a simple rhombohedral form of boron, Acta Cryst. 12, 503 (1959).

[97]McCarty, L.V. and D.R. Carpenter, J. Electrochem. Soc. 107, 38 (1960).

[98]Hoard, J.L., S. Geller, and R.E. Hughes, J. Am. Chem. Soc., 73, 1892 (1951).

[99]Hoard, J.L., R.E. Hughes, and D.E. Sands, The structure of tetragonal boron, J. Am. Chem. Soc. 80, 4507 (1958).

TABLE V

BERYLLIUM | REFERENCE STATE | Be

Reference State for Calculating ΔH_f°, ΔF_f°, and $\text{Log } K_p$: Solid from 298.15° to 1556°K, Liquid from 1556° to 2754°K, Gas from 2754° to 6000°K

gfw = 9.013 | m.p. = 1556° ± 3°K | b.p. = 2754° ± 50°K

T, °K	cal/°K gfw C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	Kcal/gfw $H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	$\text{Log } K_p$
0	0.000	0.000	Infinite	-0.467			
298.15	3.932	2.282	2.282	0.000			
300	3.951	2.307	2.283	0.007			
400	4.773	3.565	2.447	0.447			
500	5.260	4.687	2.787	0.950			
600	5.588	5.676	3.186	1.494			
700	5.846	6.557	3.606	2.066			
800	6.072	7.353	4.025	2.662			
900	6.287	8.081	4.437	3.280			
1000	6.508	8.754	4.835	3.919			
1100	6.758	9.386	5.221	4.582			
1200	7.008	9.985	5.593	5.270			
1300	7.258	10.556	5.953	5.984			
1400	7.508	11.103	6.302	6.722			
1500	7.758	11.620	6.630	7.485			
1556	7.898	11.916	6.823	7.924			
1556	7.500	13.715	6.823	10.724			
1600	7.500	13.924	7.015	11.054			
1700	7.500	14.379	7.435	11.804			
1800	7.500	14.808	7.834	12.554			
1900	7.500	15.213	8.211	13.304			
2000	7.500	15.598	8.571	14.054			
2100	7.500	15.964	8.914	14.804			
2200	7.500	16.313	9.243	15.554			
2300	7.500	16.646	9.557	16.304			
2400	7.500	16.965	9.859	17.054			
2500	7.500	17.272	10.150	17.804			
2600	7.500	17.565	10.429	18.554			
2700	7.500	17.848	10.698	19.304			
2754	7.500	17.996	10.839	19.709			
2754	4.993	43.595	10.839	90.207			
2800	4.997	43.675	11.376	90.437			
2900	5.007	43.851	12.493	90.937			
3000	5.021	44.021	13.542	91.438			
3100	5.037	44.186	14.528	91.941			
3200	5.057	44.346	15.457	92.446			
3300	5.081	44.502	16.334	92.953			
3400	5.109	44.654	17.165	93.462			
3500	5.142	44.803	17.953	93.975			
3600	5.179	44.948	18.700	94.491			
3700	5.221	45.090	19.412	95.010			
3800	5.268	45.230	20.089	95.535			
3900	5.320	45.368	20.736	96.064			
4000	5.378	45.503	21.353	96.599			
4100	5.440	45.637	21.944	97.140			
4200	5.508	45.769	22.510	97.687			
4300	5.581	45.899	23.052	98.242			
4400	5.658	46.028	23.573	98.804			
4500	5.741	46.156	24.073	99.373			
4600	5.828	46.283	24.554	99.952			
4700	5.919	46.410	25.019	100.539			
4800	6.014	46.535	25.465	101.136			
4900	6.113	46.660	25.896	101.742			
5000	6.215	46.785	26.313	102.358			
5100	6.320	46.909	26.716	102.985			
5200	6.428	47.033	27.106	103.622			
5300	6.538	47.156	27.482	104.271			
5400	6.649	47.279	27.848	104.930			
5500	6.763	47.402	28.202	105.601			
5600	6.877	47.525	28.546	106.283			
5700	6.993	47.648	28.880	106.976			
5800	7.108	47.771	29.205	107.681			
5900	7.224	47.893	29.520	108.398			
6000	7.340	48.016	29.828	109.126			

BERYLLIUM REFERENCE STATE

SUMMARY OF UNCERTAINTY ESTIMATES

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	± .050	±.020	±.020	± .000			
1000	± .060	±.070	±.030	± .040			
1556	± .240	±.160	±.050	± .150			
1556	± .380	±.470	±.050	± .650			
2000	±1.040	±.640	±.160	± .960			
2754	±2.170	±.990	±.200	±2.170			

TABLE VI

BERYLLIUM — IDEAL MONATOMIC GAS — Be

Reference State for Calculating ΔH_f°, ΔF_f°, and $\text{Log}\,K_p$: Solid from 298.15° to 1556°K, Liquid from 1556° to 2754°K, Gas from 2754° to 6000°K.

gfw = 9.013 — m.p. = 1556° ± 3°K — b.p. = 2754° ± 50°K

	cal/°K gfw			Kcal/gfw			
T,°K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-1.481	76.986	76.986	Infinite
298.15	4.968	32.545	32.545	0.000	78.000	68.977	-50.559
300	4.968	32.576	32.545	0.009	78.002	68.921	-50.206
400	4.968	34.005	32.740	0.506	78.059	65.883	-35.995
500	4.986	35.114	33.108	1.003	78.053	62.839	-27.466
600	4.968	36.020	33.520	1.500	78.006	59.800	-21.781
700	4.968	36.785	33.933	1.996	77.930	56.770	-17.724
800	4.968	37.449	34.332	2.493	77.831	53.754	-14.684
900	4.968	38.034	34.712	2.990	77.710	50.752	-12.324
1000	4.968	38.557	35.070	3.487	77.568	47.765	-10.439
1100	4.968	39.031	35.409	3.984	77.402	44.792	-8.899
1200	4.968	39.463	35.729	4.481	77.211	41.837	-7.619
1300	4.968	39.861	36.032	4.977	76.993	38.896	-6.539
1400	4.968	40.229	36.319	5.474	76.752	35.976	-5.616
1500	4.968	40.572	36.591	5.971	76.486	33.058	-4.816
1556	4.968	40.754	36.738	6.249	76.325	31.452	-4.417
1556	4.968	40.754	36.738	6.249	73.525	31.452	-4.417
1600	4.968	40.892	36.850	6.468	73.414	30.265	-4.134
1700	4.968	41.194	37.097	6.965	73.161	27.575	-3.545
1800	4.968	41.478	37.332	7.461	72.907	24.901	-3.023
1900	4.968	41.746	37.558	7.958	72.654	22.241	-2.558
2000	4.969	42.001	37.774	8.455	72.401	19.595	-2.141
2100	4.969	42.244	37.981	8.952	72.148	16.960	-1.765
2200	4.970	42.475	38.180	9.449	71.895	14.339	-1.424
2300	4.972	42.696	38.371	9.946	71.642	11.727	-1.114
2400	4.974	42.907	38.556	10.443	71.389	9.128	-0.831
2500	4.977	43.110	38.734	10.941	71.137	6.542	-0.572
2600	4.982	43.306	38.906	11.439	70.885	3.958	-0.333
2700	4.988	43.494	39.073	11.937	70.633	1.389	-0.112
2754	4.993	43.595	39.163	12.207	70.498	0.000	0.000
2754	4.993	43.595	39.163	12.207			
2800	4.997	43.675	39.234	12.437			
2900	5.007	43.851	39.390	12.937			
3000	5.021	44.021	39.542	13.438			
3100	5.037	44.186	39.689	13.941			
3200	5.057	44.346	39.832	14.446			
3300	5.081	44.502	39.971	14.953			
3400	5.109	44.654	40.106	15.462			
3500	5.142	44.803	40.238	15.975			
3600	5.179	44.948	40.367	16.491			
3700	5.221	45.090	40.493	17.010			
3800	5.268	45.230	40.616	17.535			
3900	5.320	45.368	40.736	18.064			
4000	5.378	45.503	40.853	18.599			
4100	5.440	45.637	40.968	19.140			
4200	5.508	45.769	41.081	19.687			
4300	5.581	45.899	41.192	20.242			
4400	5.658	46.028	41.300	20.804			
4500	5.741	46.156	41.407	21.373			
4600	5.828	46.283	41.511	21.952			
4700	5.919	46.410	41.614	22.539			
4800	6.014	46.535	41.715	23.136			
4900	6.113	46.660	41.815	23.742			
5000	6.215	46.785	41.913	24.358			
5100	6.320	46.909	42.010	24.985			
5200	6.428	47.033	42.105	25.622			
5300	6.538	47.156	42.199	26.271			
5400	6.649	47.279	42.292	26.930			
5500	6.763	47.402	42.384	27.601			
5600	6.877	47.525	42.475	28.283			
5700	6.993	47.648	42.565	28.976			
5800	7.108	47.771	42.653	29.681			
5900	7.224	47.893	42.741	30.398			
6000	7.340	48.016	42.828	31.126			

BERYLLIUM IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	cal/°K gfw C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	Kcal/gfw $H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	±.000	±.002	±.002	±.000	± .500	± .510	±.370
1000	±.000	±.002	±.002	±.000	± .540	± .530	±.120
1556					± .650	± .580	±.080
1556					±1.150	± .580	±.080
2000	±.000	±.002	±.003	±.000	±1.460	± .820	±.090
2754					±2.670	±1.050	±.090
3000	±.001	±.002	±.003	±.001			
4000	±.002	±.003	±.003	±.002			
5000	±.002	±.003	±.003	±.004			
6000	±.002	±.003	±.004	±.005			

TABLE VII

REPORTED MELTING POINTS OF BORON

°C	°K	Original Reference	Quoting Reference No.
2400	2673	Weintraub[112]	106
2300	2573	Probably ICT* or Weintraub [112]	102, 109
2200	2473	Tride and Birnbrauer[111]	110
>2147	>2420	Searcy and Myers[104]	---
2100-2200	(2373-2473)	Cooper[106]	---
2130 ± 10	2403 ± 10	Piper[108]	---
2130	2403	Cline[105]	---
2040	2313	Cueilleron[100]	103, 113
2000-2075	2273-2448	Cueilleron[107]	77, 106

*International Critical Tables[101] give the figure as 2300°C, implying that the melting point is somewhere between 1800° and 2800°C.

100 Cueilleron, J., Ann. chim. 19, 459 (1944).

101 International Critical Tables, Vol. I, (1926), p. 103.

102 Hodgman, C.D., R.C. Weast, and S.M. Selby, Handbook of Chemistry and Physics, 40th ed., Chem. Rubber Pub. Co., Cleveland (1958-59), p. 544.

103 Lange, A.L. and G.M. Forker, Handbook of Chemistry, 9th ed., Handbook Pub., Sandusky, Ohio (1956).

104 Searcy, A.W. and C.E. Myers, J. Phys. Chem. 61, 957 (1957).

105 Cline, C.F., An investigation of the compound silicon boride (SiB_6), J. Electrochem. Soc. 106 (4), 332 (1959).

106 Cooper, H.S., In: Rare Metals Handbook, C.A. Hampel, ed., Reinhold, N.Y. (1954), p. 78.

107 Cueilleron, J., The melting point of boron, Compt. Rend. 221, 698 (1945).

108 Piper, E.L., Research Study to Determine the Phase Equilibrium Relations of Selected Metal Carbides at High Temperatures, Natl. Carbon Research Labs., Prog. Rept. 1, Contract AF33(616)-6286, Task No. 73500 (30 June 1959).

109 Forsythe, W.E., Smithsonian Tables, Vol. 120, 9th ed. Rev., Smithsonian Inst. Pub., Washington (1956), 827 p.

110 Laubengayer, A.W., A.E. Newkirk, and R.L. Brandaur, J. Chem. Education 19, 382 (1942).

111 Tride and Birnbrauer, Z. anorg. u. allgem. Chem. 87, 129 (1941).

112 Weintraub, E.J., Ind. Eng. Chem. 5, 106 (1913).

113 Natl. Bur. Standards (US) circ 500, Series I and II (1952).

In evaluating these various melting-point data, the most important consideration is probably sample purity. Usually, small amounts of impurities are expected to lower the melting point, and cause an increase in the melting-point range. The highest values in Table VII (from 2200° to 2400°C) are based on very old work, and were not given serious consideration. The values of Cueilleron[100, 107] appear to be too low in the light of the more recent work. The values from references 104-106 and 108 in Table VII should be considered in more detail.

TABLE VIII

SUMMARY OF RECENT BORON MELTING-POINT DATA

Reference	Type of Boron	Purity (percent)	Melting Point (°K)
Searcy and Myers[104]	Fairmount amorphous, sublimed.	98.9 99.95	> 2420
Cline[105]	Pacific Coast Borax, "fused."	95-97	2403
Cooper[106]	Briquette.	---	2373-2473
Piper[108]	Pacific Coast Borax, powder.	98.9	2403 ± 10

The work of Searcy and Myers[104] seems to be the most reliable since some of their samples had purities up to 99.95 percent. Since they could still not obtain fusion at 2420°K, it is necessary to estimate the melting point. In view of the lower, recent values given in references 105 and 108, it would seem that the melting point could not be much higher than 2420°K. Accordingly, the melting point was taken to be 2450° ± 50°K, which would encompass these recent values.

c. Thermodynamic Data

For crystalline boron as the reference state, the data of Wise, Margrave, and Altman[17] to 2400°K have been used in the present report. Their values were based on the low-temperature data of Johnston et al,[114] and their own measurements to 1200°K. They have extrapolated these data to 2400°K. Their data have been extrapolated here to the estimated melting point of 2450°K. For the heat of fusion, the

[114] Johnston, H.L., H.N. Hersh, and E.C. Kerr, J. Am. Chem. Soc. 73, 1112 (1951).

Sinke *et al*[32] procedure has been followed to obtain an entropy of melting of 2.3 e.u., or a heat of fusion of 5635 cal/g atom. Similarly, the liquid heat capacity has been estimated as 7.5 cal/°K g atom.

d. Sublimation Data

The available data for the sublimation of boron showed considerable uncertainty also (see Table IX).

TABLE IX

BORON SUBLIMATION DATA (Kcal/g atom)

Reference	Method	ΔH°_{s298}	ΔH°_{s0}
Searcy and Myers[104]	Effusion	139 ± 4	137.7 (see reference 117)
Robson[115]	Effusion	135.0	133.8 ± 0.7
Thorn,[116] and Evans *et al*[117]	---	---	133
Chupka *et al*[118] and Leitnaker[119]	Mass spectrometer	129	128.3 (see reference 117)
Schissel and Williams[120]	Mass spectrometer	129 ± 5	---
Akishin *et al*[121]	Mass spectrometer	---	131.6 ± 5

[115] Robson, H.R., Ph. D. Thesis, Univ. of Kansas, Lawrence (1958).

[116] Thorn, R.J., Private Communication to Evans *et al*[117].

[117] Evans, W.H., D.D. Wagman, and E.J. Prosen, The Vapor Pressure of Some Boron Compounds, Natl. Bur. Standards (U.S.), Rept. 5663 (23 December 1957), Thermodynamic Properties of Some Boron Compounds, Natl. Bur. Standards (U.S.), Rept. 4943 (31 August 1956).

[118] Chupka, W.A. to P.O. Schissel and W.S. Williams, Quoted in Reference 119.

[119] Leitnaker, J.M., Thermodynamic Properties of Refractory Borides, Los Alamos Sci. Lab. LA-2402 (TID-4500), (13 April 1960).

[120] Schissel, P.O. and W.S. Williams, Mass spectrometric study of the vaporization of certain refractory compounds, Bull. Am. Phys. Soc. 4, 139 (1959).

[121] Akishin, P.A., D.O. Nikitin, and L.N. Gorokhov, Determination of the heat of sublimation of boron by mass spectrometry, Dokl. Akad. Nauk, SSSR (Proc. Acad. Sci. USSR) 129, 1075 (1959).

e. Calculations

1) Condensed phases

Wise, Margrave, and Altman[17] have tabulated values of C_p°, $H_T^\circ - H_0^\circ$, $-\left(\frac{F_T^\circ - H_0^\circ}{T}\right)$, and S_T° from 100° to 2400°K. These values were converted to the standard reference temperature of 298°K according to equations (107) through (110). $H_{298}^\circ - H_0^\circ = 290.4$ cal/gfw was taken from that reference.[17]

The formula given by Wise, Margrave, and Altman,[17] (see eq. (20) and its discussion)

$$C_p^\circ/R = D(\theta_D/T) + 2\,E_1(\theta_1/T) + E_2(\theta_2/T)\,, \qquad (132)$$

was used to obtain the C_p° value at 2450°K by extrapolation. It was used as in equation (133) with available tabulations of $D(\theta_D/)T$ and $E(\theta/T)$ with the reported values of θ_D, θ_1 and θ_2.

$$C_p^\circ/R = D(\theta_D/T) + 2\,E(\theta_1/T) + E(\theta_2/T). \qquad (133)$$

The Einstein functions $E(\theta_1/T)$ and $E(\theta_2/T)$ were evaluated from the tables of Sherman and Ewell,[12] and the Debye function $D(\theta_D/T)$ was evaluated from the tables of Taylor and Glasstone which give $3RD(\theta_D/T)$.[122] The C_p° and other values in Table X, calculated from this formula at 2450°K, were in good agreement with those obtained by extrapolation of Wise, Margrave, and Altman's[17] table by a difference method.

At the chosen melting point, 2450°K, the value of $C_p^\circ = 7.50$ was taken for the reasons discussed in section c. above. Similarly, the heat of fusion was taken to be 5635 cal/g atom, and the entropy of melting was taken to be 2.3 e.u. Hence, the quantities $H_T^\circ - H_{298}^\circ$ and S_T° had the respective increments of 5635 and 2.3 for the liquid phase at 2450°K.

For temperatures above 2450°K, the heat capacity was assumed to be constant at 7.50 cal/$^\circ$K g atom. Therefore, $H_T^\circ - H_{298}^\circ$ became

$$H_T^\circ - H_{298}^\circ = \left[H_{2450}^\circ(\text{liq}) - H_{298}^\circ\right] + 7.5\,(T - 2450). \qquad (134)$$

[122] Taylor, H.S. and S. Glasstone, A Treatise on Physical Chemistry, Vol. I: Atomistics and Thermodynamics, Van Nostrand, N.Y. (1942), p. 669.

TABLE X

BORON | REFERENCE STATE | B

Reference State for Calculating ΔH_f°, ΔF_f°, and Log K_p : Solid from 298.15° to 2450°K, Liquid from 2450° to 6000°K (Metastable above b.p.).

gfw = 10.82 | m.p. = 2450° ± 50°K | b.p. = 3970° ± 250°K*

T, °K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal/gfw)	ΔH_f° (Kcal/gfw)	ΔF_f° (Kcal/gfw)	Log K_p
0	0.000	0.000	Infinite	−0.290			
298.15	2.823	1.392	1.392	0.000			
300	2.845	1.409	1.389	0.006			
400	3.841	2.374	1.516	0.343			
500	4.498	3.307	1.783	0.762			
600	4.966	4.170	2.108	1.237			
700	5.333	4.964	2.461	1.752			
800	5.639	5.697	2.820	2.301			
900	5.902	6.377	3.178	2.879			
1000	6.130	7.011	3.530	3.481			
1100	6.329	7.605	3.874	4.104			
1200	6.502	8.163	4.208	4.746			
1300	6.652	8.689	4.532	5.403			
1400	6.783	9.187	4.847	6.075			
1500	6.897	9.659	5.153	6.759			
1600	6.996	10.107	5.448	7.454			
1700	7.083	10.534	5.735	8.158			
1800	7.160	10.941	6.013	8.870			
1900	7.228	11.330	6.282	9.590			
2000	7.288	11.703	6.545	10.316			
2100	7.341	12.059	6.798	11.047			
2200	7.388	12.402	7.045	11.784			
2300	7.430	12.731	7.285	12.525			
2400	7.468	13.048	7.519	13.269			
2450	7.485	13.222	7.654	13.642			
2450	7.500	15.522	7.654	19.277			
2500	7.500	15.673	7.812	19.652			
2600	7.500	15.967	8.120	20.402			
2700	7.500	16.250	8.416	21.152			
2800	7.500	16.523	8.701	21.902			
2900	7.500	16.786	8.975	22.652			
3000	7.500	17.041	9.240	23.402			
3100	7.500	17.287	9.496	24.152			
3200	7.500	17.525	9.743	24.902			
3300	7.500	17.756	9.982	25.652			
3400	7.500	17.979	10.214	26.402			
3500	7.500	18.197	10.439	27.152			
3600	7.500	18.408	10.658	27.902			
3700	7.500	18.614	10.870	28.652			
3800	7.500	18.814	11.077	29.402			
3900	7.500	19.009	11.277	30.152			
4000	7.500	19.199	11.473	30.902			
4100	7.500	19.384	11.664	31.652			
4200	7.500	19.565	11.850	32.402			
4300	7.500	19.741	12.031	33.152			
4400	7.500	19.913	12.208	33.902			
4500	7.500	20.082	12.382	34.652			
4600	7.500	20.247	12.551	35.402			
4700	7.500	20.408	12.716	36.152			
4800	7.500	20.566	12.878	36.902			
4900	7.500	20.721	13.037	37.652			
5000	7.500	20.872	13.192	38.402			
5100	7.500	21.021	13.344	39.152			
5200	7.500	21.167	13.493	39.902			
5300	7.500	21.309	13.639	40.652			
5400	7.500	21.450	13.783	41.402			
5500	7.500	21.587	13.923	42.152			
5600	7.500	21.723	14.062	42.902			
5700	7.500	21.855	14.197	43.652			
5800	7.500	21.986	14.330	44.402			
5900	7.500	22.114	14.461	45.152			
6000	7.500	22.240	14.590	45.902			

*Estimated from change of sign of ΔF_f° in ideal gas table.

BORON REFERENCE STATE

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	cal/°K gfw			Kcal/gfw			
	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	± .200	± .020	±.020	± .000			
1000	± .200	± .260	±.120	± .140			
2000	± .200	± .400	±.230	± .340			
2450	± .200	± .420	±.250	± .430			
2450	±1.000	± .720	±.250	±1.160			
3000	±1.000	± .920	±.350	±1.710			
4000	±1.000	±1.200	±.520	±2.710			
5000	±1.000	±1.430	±.690	±3.710			
6000	±1.000	±1.610	±.830	±4.710			

TABLE XI

BORON — IDEAL MONATOMIC GAS — B

Reference State for Calculating ΔH_f°, ΔF_f°, and $\text{Log } K_p$: Solid from 298.15° to 2450°K, Liquid from 2450° to 6000°K (Metastable above b.p.).

gfw = 10.82 — m.p. = 2450° ± 50°K — b.p. = 3970°± 250°K

T, °K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal/gfw)	ΔH_f° (Kcal/gfw)	ΔF_f° (Kcal/gfw)	Log K_p
0	0.000	0.000	Infinite	-1.511	131.779	131.779	Infinite
298.15	4.971	36.649	36.649	0.000	133.000	122.489	-89.782
300	4.971	36.680	36.650	0.009	133.003	122.422	-89.180
400	4.970	38.110	36.845	0.506	133.163	118.869	-64.943
500	4.969	39.218	37.212	1.003	133.241	115.286	-50.389
600	4.969	40.124	37.624	1.500	133.263	111.691	-40.681
700	4.969	40.890	38.037	1.997	133.245	108.097	-33.747
800	4.968	41.554	38.436	2.494	133.193	104.508	-28.548
900	4.968	42.139	38.815	2.991	133.112	100.927	-24.507
1000	4.968	42.662	39.175	3.487	133.006	97.355	-21.275
1100	4.968	43.136	39.514	3.984	132.880	93.796	-18.634
1200	4.968	43.568	39.833	4.481	132.735	90.250	-16.435
1300	4.968	43.966	40.136	4.978	132.575	86.715	-14.577
1400	4.968	44.334	40.423	5.475	132.400	83.194	-12.986
1500	4.968	44.677	40.695	5.972	132.213	79.687	-11.609
1600	4.968	44.998	40.955	6.468	132.014	76.189	-10.406
1700	4.968	45.299	41.202	6.965	131.807	72.707	-9.346
1800	4.968	45.583	41.437	7.462	131.592	69.237	-8.406
1900	4.968	45.851	41.662	7.959	131.369	65.778	-7.565
2000	4.968	46.106	41.878	8.446	131.140	62.334	-6.811
2100	4.968	46.349	42.086	8.952	130.905	58.896	-6.129
2200	4.968	46.580	42.285	9.449	130.665	55.472	-5.510
2300	4.968	46.801	42.476	9.946	130.421	52.061	-4.946
2400	4.968	47.012	42.660	10.443	130.174	48.662	-4.431
2450	4.968	47.114	42.750	10.691	130.049	47.015	-4.193
2450	4.968	47.114	42.750	10.691	124.414	47.015	-4.193
2500	4.968	47.215	42.839	10.940	124.288	45.433	-3.971
2600	4.968	47.410	43.011	11.437	124.035	42.284	-3.554
2700	4.968	47.597	43.177	11.933	123.781	39.146	-3.168
2800	4.968	47.778	43.338	12.430	123.528	36.017	-2.811
2900	4.969	47.952	43.494	12.927	123.275	32.895	-2.478
3000	4.969	48.121	43.646	13.424	123.022	29.782	-2.169
3100	4.969	48.284	43.793	13.921	122.769	26.680	-1.880
3200	4.970	48.441	43.935	14.418	122.516	23.586	-1.610
3300	4.970	48.594	44.074	14.915	122.263	20.497	-1.357
3400	4.971	48.743	44.210	15.412	122.010	17.414	-1.119
3500	4.972	48.887	44.341	15.909	121.757	14.343	-0.895
3600	4.973	49.027	44.469	16.406	121.504	11.281	-0.684
3700	4.975	49.163	44.594	16.904	121.252	8.222	-0.485
3800	4.977	49.296	44.716	17.401	120.999	5.172	-0.297
3900	4.979	49.425	44.835	17.899	120.747	2.124	-0.119
4000	4.982	49.551	44.951	18.397	120.495	-0.912	0.049
4100	4.985	49.674	45.066	18.896	120.244	-3.948	0.210
4200	4.988	49.794	45.176	19.394	119.992	-6.969	0.362
4300	4.993	49.912	45.285	19.893	119.741	-9.992	0.507
4400	4.997	50.027	45.392	20.393	119.491	-13.009	0.646
4500	5.002	50.139	45.496	20.893	119.241	-16.013	0.777
4600	5.008	50.249	45.598	21.393	118.991	-19.016	0.903
4700	5.015	50.357	45.698	21.894	118.742	-22.015	1.023
4800	5.022	50.463	45.797	22.396	118.494	-25.011	1.138
4900	5.030	50.566	45.892	22.899	118.247	-27.989	1.248
5000	5.038	50.668	45.987	23.402	118.000	-30.975	1.353
5100	5.048	50.768	46.080	23.906	117.754	-33.953	1.454
5200	5.058	50.866	46.171	24.412	117.510	-36.925	1.551
5300	5.069	50.962	46.260	24.918	117.266	-39.891	1.644
5400	5.081	51.057	46.348	25.426	117.024	-42.851	1.734
5500	5.093	51.151	46.435	25.934	116.782	-45.816	1.820
5600	5.107	51.242	46.519	26.444	116.542	-48.759	1.902
5700	5.121	51.333	46.603	26.956	116.304	-51.714	1.982
5800	5.136	51.422	46.686	27.468	116.066	-54.664	2.059
5900	5.152	51.510	46.767	27.983	115.831	-57.605	2.133
6000	5.168	51.597	46.847	28.499	115.597	-60.542	2.205

BORON IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	cal/°K gfw			Kcal/gfw			
	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	±.001	±.001	±.001	±.000	±4.000	±4.000	±2.930
1000	±.001	±.001	±.001	±.001	±4.140	±4.120	± .900
2000	±.001	±.001	±.001	±.002	±4.340	±4.460	± .480
2450	±.001	±.001	±.001	±.002	±4.430	±4.610	± .410
2450	±.001	±.001	±.001	±.002	±5.160	±4.610	± .410
3000	±.001	±.001	±.001	±.003	±5.710	±5.050	± .360
4000	±.001	±.001	±.001	±.004	±6.710	±6.080	± .330
5000	±.001	±.001	±.001	±.005	±7.710	±7.450	± .320
6000	±.001	±.001	±.001	±.006	±8.720	±8.980	± .320

The entropy was calculated according to equation (107) which reduced to equation (135),

$$S^\circ_T = S^\circ_{2450}\,(\mathrm{liq}) + 17.2693 \log_{10} \frac{T}{2450} \tag{135}$$

The free-energy function was calculated according to equation (108). The reference state functions are summarized in Table X.

2) Gas phase

Wilkins and Altman[123] tabulated C°_p, $H^\circ_T - H^\circ_0$, and S°_T in the range from 0° to $6000^\circ K$ at $100^\circ K$ intervals. All these values were used as tabulated. The enthalpy (heat content) and free-energy functions were calculated from equations (108) and (110). The remaining functions were calculated from equations (42), (43), and (44). The ideal gas functions are summarized in Table XI.

3) Error analyses

a) Uncertainty estimates in condensed phase functions are given on the back of Table X.

1 Heat capacity

In the case of boron, C°_p data from more than one source have been available for comparison. They are summarized in Table XII.

TABLE XII

BORON HEAT CAPACITY DATA FROM VARIOUS SOURCES

Source	C°_p (cal/°K g atom)	
	298.15°K	2000°K
Wise *et al*[17]	2.823	7.288
Sinke and Stull[32]	2.63	7.20
Evans *et al*[117]	2.650	---

[123] Wilkins, R.L. and R.L. Altman, J. Chem. Phys. 31, 337 (1959).

It can be immediately seen from Table XII that there is a spread of about 0.20 cal/^{o}K g atom in the values of heat capacity at room temperature. Although the measurements of Wise et al[17] were made on crystalline samples, whereas the others apparently used "amorphous" boron, the results of the former measurements could not be simply accepted since it would appear that their samples were not from a pure, single phase. For example, they made the statement that "some of the high temperature β- rhombohedral form" was present in all samples. A conservative evaluation therefore would require assuming that their samples contained a mixture of phases and adopting an uncertainty of 0.2 cal/g atom ^{o}K for the room-temperature heat capacity of boron. In the absence of any better information, the same uncertainty was assigned to the heat capacity at 2000^{o}K even though the agreement between values from the two sources was better at that temperature.

For the liquid, a value of C_p^o = 7.50 cal/^{o}K g atom and an uncertainty in this value (as well as $\Delta C_p^\bullet$) equal to 1.0 cal/^{o}K g atom was simply assumed.

2 Entropy

Uncertainty ranges were calculated from equation (115) with δC_p^o equal to 0.2 cal/^{o}K gfw in the temperature range from 298.15^{o} to 2450^{o}K.

An uncertainty of 0.3 e.u. was assumed for the entropy of fusion of boron.

In the melt (2450^{o} < T < 6000^{o}K), the uncertainty in heat capacity was assumed to be 1.0 cal/^{o}K gfw.

3 Enthalpy

Uncertainty range calculations were made with equation (118).

4 Free Energy function

Free energy function uncertainty range calculations were made with equation (120).

5 Uncertainty in gas phase functions

The effect of energy assignments on ideal gas function accuracy has been briefly considered by Kolsky, Gilmer, and Gilles.[51]

On the basis of their analysis, it appears that the energy levels of B(g) are well-established and that their small uncertainty causes an error of only ± 0.0002 cal/°K g atom in C_p^o for the ideal gas. It is also reassuring to compare the available C_p^o data from two separate tabulations.

Temperature (°K)	Values* of Wilkins *et al*[123]	Values* of Kolsky *et al*[51]	Difference*
298.15	4.971	4.9709**	0.0001
6000	5.168	5.1683**	0.0003

Thus, one can conclude conservatively that these C_p^o data are accurate at least to ± 0.001 cal/°K g atom.

A similar analysis of those authors[123, 51] entropy data shows that S_T^o is also accurate to ± 0.001 cal/°K g atom.

Temperature (°K)	Values* of Wilkins *et al*[123]	Values* of Kolsky *et al*[51]	Difference*
298.15	36.649	36.648**	0.001
6000	51.597	51.5959**	0.0011

Free-energy and entropy functions calculated from these data have insignificant uncertainties for most practical purposes.

The uncertainties in ΔH_f^o, ΔF_f^o, and $\log_{10} K_p$ are much greater. These uncertainties are obtained from equations (42), (43), and (44).

*Cal/°K g atom.
**Converted to chemical atomic-weight scale.

The uncertainty estimates on the back of Table XI are slightly conservative in that the uncertainty in the heat of sublimation at 298°K has been used for all other temperatures. Since heats of sublimation of boron have been obtained from high-temperature (near 2000°K) experiments, it is reasonable to expect the values in the neighborhood of 2000°K to be more precise than the value at 298°K. Actually, the difference in uncertainties at these two temperatures is less than 0.5 kcal/g atom. This is small compared to the total error in the heat of sublimation.

3. Calcium

a. Crystal Structure, Transition Point, and Melting Point

Elemental calcium was shown by Smith, Carlson, and Vest[124] to have a face-centered,cubic structure from room temperature to 737°K and to transform at the latter temperature to a body-centered form stable up to the melting point.

These results are in contrast with those of earlier work from which the existence of additional allotropic modifications of calcium was inferred. Both a "low symmetry" or "complex" phase[125] and a hexagonal, close-packed phase had been previously reported.[125-128]

The transition temperatures and phase stabilities had been found to depend on the thermal history of the calcium samples. Smith, Carlson, and Vest[124] concluded that the additional phases were due to impurities. Schottmiller, King, and Kanda[129] later also reported the two additional phases and suggested that small amounts of impurities (presumably metallic) could nucleate a transformation that occurred only very slowly in highly pure calcium. However, Smith and Bernstein[130] subsequently concluded that nitrogen or carbon induced the formation of the "low symmetry" phase and that hydrogen was responsible for the formation of the hexagonal close-packed phase. The matter has probably not been unambiguously resolved to everyone's satisfaction because the impurities responsible are difficult to control and are relatively difficult to determine quantitatively.

The results of Smith, Carlson, and Vest[124] have been accepted, and 737° ±10°K has been adopted as the transition temperature for the present project. Stull and Sinke[77] and Kelley[56] adopted a transition temperature of 713°K from the earlier review of Kubaschewski *et al.*[79]

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[124] Smith, J., O. Carlson, and R. Vest, J. Electrochem. Soc. 103, 409 (1956).

[125] Graf, L., Physik Z. 35, 551 (1934).

[126] Evert, F., H. Hartmann, and H. Peisker, Z. anorg. u. allgem. Chem. 213, 126 (1933).

[127] Schulze, A., Physik Z. 36, 595 (1935).

[128] Meisert, H., T.J. Tiedema, and W.G. Burgers, Acta Cryst. 9, 525 (1956).

[129] Schottmiller, J., A. King, and F. Kanda, J. Phys. Chem. 62, 1446 (1958).

[130] Smith, J. and B. Bernstein, J. Electrochem. Soc. 106, 448 (1959).

The melting point of calcium used here, 1123° ± 10°K, was listed by Kubaschewski et al,[79] and was also used in other recent compilations.[56, 76, 77] The more reliable values reported range from 1116° to 1124°K.[125, 129, 131-133]

b. Thermodynamic Properties

1) Heat of transition

The heat of transition of face-centered cubic calcium to body-centered cubic calcium was taken as 240 ± 60 cal/gfw. This value was recommended by Kubaschewski et al[79] from the heat content measurements of Moser and Schulze[127] (212 cal/gfw), Jauch[134] (240 ± 60 cal/gfw), and the thermal analysis results of Rinck[135] (275 cal/gfw). Eastman, Williams, and Young[136] reported the heat of transition to be 100 ± 25 cal/gfw from their heat content measurements. It was assumed that a change of the transition temperature from the previously accepted 713° to 737°K alters the heat of transition within the uncertainty given above.

2) Heat of fusion

Kubaschewski et al[79] list the heat of fusion of calcium as 2070 ± 100 cal/gfw. This value is based on Jauch's[134] heat content measurements and was adopted here. Kelley[137] arrived at a value of 2230 ± 300 cal/gfw from a review of phase diagrams of calcium alloys. Other determinations of the heat of fusion of calcium have been made by Zalesinski and Zulinski[138] (3150 cal/gfw, 3000 cal/gfw) and by Rinck[135] (1640 cal/gfw).

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[131] Antropoff, A. von and E. Falk, Z. anorg. u. allgem. Chem. 187, 405 (1930).

[132] Hoffmann, F. and A. Schulze, Physik Z. 36, 453 (1935).

[133] Weibke, F. and W. Bartels, Z. anorg. u. allgem. Chem. 218, 241 (1934).

[134] Jauch, R. Diplomarbeit, Techn. Hochschule, Stuttgart (1946).

[135] Rinck, E., Ann. Chim. (10) 18, 510 (1932).

[136] Eastman, E.D., A.M. Williams, and T.F. Young, J. Am. Chem. Soc. 46, 1178 (1924).

[137] Kelley, K.K., Bureau of Mines Bull. 393 (1936).

[138] Zalesinski, E. and R. Zulinski, Bull. Int. Polon. Sci. Lettres (A), p. 479 (1928).

3) Entropy and heat content at 298.15°K

Kelley[139] gave the entropy of elemental calcium at 298.16°K as 9.95 ± 0.10 cal/°Kgfw, based almost entirely on the low-temperature heat capacity data of Clusius and Vaughen[140] (10° to 201°K). Hultgren[76] arrived at the same value from these data plus the heat capacity measurements of Griffel, Vest, and Smith[141] (1.8° to 4.2°K), and Roberts[142] (1.5° to 20°K). $H^o_{298} - H^o_0$ was calculated by the present authors to be 1375 cal/gfw for the solid.

Other low temperature heat capacity measurements on calcium include those of Gunther[143] (22° to 62°K), and of Eastman and Rodebush[144] (68° to 294°K).

4) High-temperature heat content

The heat capacity and heat content of elemental calcium are not very well-known. The only available low-temperature heat capacity data, those of Clusius and Vaughen,[140] terminate at 201°K and have been extrapolated to a value of 6.28 cal/°K gfw at 298.15°K. Above room temperature, data were derived from the heat content measurements of Eastman, Williams, and Young[136] (373° to 878°K), and of Jauch[134] (298° to 1223°K). For the face-centered cubic phase, heat capacities derived from the first source are 0.25 to 0.35 cal/°K gfw higher than those from the second source over the entire range of stability from room temperature to 737°K. Extrapolation of an algebraic expression for the data of Eastman, Williams, and Young[136] to 298.15°K gave a heat capacity of 6.20 cal/°K gfw.

For purposes of the present compilation, the following algebraic expression for the heat capacity of α-Ca in cal/°K gfw was used over the temperature range from 298.15 to 737°K.

$$C^o_p = 5.205 + 3.605 \times 10^{-3}T. \qquad (136)$$

[139] Kelley, K.K., Bureau of Mines Bull. 477 (1950).

[140] Clusius, K. and J. V. Vaughen, J. Am. Chem. Soc. 52, 4684 (1930).

[141] Griffel, M., R.W. Vest, and J.F. Smith, J. Chem. Phys. 27, 1267 (1957).

[142] Roberts, L.M., Proc. Roy. Soc. (London) 70B, 738 (1957).

[143] Gunther, P., Ann. Physik 51, 828 (1916).

[144] Eastman, E.D. and W.H. Rodebush, J. Am. Chem. Soc. 40, 489 (1918).

This expression gives a heat capacity of 6.28 cal/°K gfw at 298.15°K and an average value of the results of Eastman, Williams and Young,[136] and Jauch[134] extrapolated to 737°K. This expression is slightly different from others which have been used elsewhere.[56, 76, 77]

An algebraic representation of the heat content measurements of Jauch in cal/°K gfw over the temperature range from 737° to 1123°K was the basis for the calculation of thermodynamic functions of body-centered cubic β-Ca.

$$C_p^o = 1.50 + 7.74 \times 10^{-3} T + 2.5 \times 10^5 \; T^{-2}. \qquad (137)$$

These data have also been accepted elsewhere[56, 76, 77] with slight modification. The heat capacities of β-Ca derived from the data of Eastman, Williams, and Young[136] (to 878°K) are considerably lower than the accepted values. Zalesinski and Zulinski[138] are in better agreement with Jauch[134] than with Eastman, Williams, and Young.[136]

Other sources for high-temperature heat capacity or heat content data for solid calcium are Bernini[145] (273° to 430°K), Bunsen[146] (273° to 373°K), and Schulze[127] (723° to 803°K).

Jauch's[134] value for the heat capacity of liquid calcium, 7.40 cal/°K gfw, was adopted on the basis of measurements of heat content from the melting point to 950°K. This value has been used to the boiling point with increasing assigned uncertainty. Zalesinski and Zulinski[138] reported the heat capacity of liquid calcium to be 10.7 cal/°K gfw. Jauch's[134] value was preferred because it was more consistent with the heat capacity of liquid magnesium, 7.8 cal/°K gfw(See section IV-A8).

5) Heat of formation of the monatomic gas

Free-energy functions tabulated herein were used with vapor pressure data from the following sources to calculate the indicated heats of formation at 298.15°K using the Third Law Method:

[145] Bernini, A., Physik Z. 7, 168 (1906).

[146] Bunsen, R., Poggendorf's Ann. 141, 1 (1879).

Source	Temperature Range (°K)	ΔH°_{f298} (Kcal/gfw)
Priselkov and Nesmeyanov[147]	748 - 943	42.200 ± 0.200
Hartmann and Schneider[148]	1254 - 1546	42.140 ± 0.400
Douglas[149]	807 - 918	42.310 ± 0.350
Tomlin[150]	801 - 877	42.230 ± 0.200
Pilling[151]	775 - 973	42.220 ± 0.650
Smith and Smythe[152]	730 - 965	43.010 ± 0.350
Ruff and Hartmann[153]	1233 - 1380	41.060 ± 3.000
Rudberg[154]	774 - 897	46.060 ± 0.350
Pidgeon and Atkinson[155]	1401 - 1477	54.520 ± 0.700

The data of Smith and Smythe[152] were derived from an algebraic representation of their results. The heat of formation tabulated from the results of Pidgeon and Atkinson[155] has been taken from Hultgren.[76] Original data points were used from the remaining sources. The results of Rudberg[154] and Pidgeon and Atkinson[155] were excluded in arriving at an average value of 42.220 Kcal/gfw to which an uncertainty of 0.250 Kcal/gfw was assigned.

[147] Priselkov, Y. and A. Nesmeyanov, Doklady Akad. Nauk SSSR 95, 1207 (1954).

[148] Hartmann, H. and R. Schneider, Z. anorg. Chem. 180, 275 (1929).

[149] Douglas, P.E., Proc. Phys. Soc. (London) 67B, 783 (1954).

[150] Tomlin, D.H., Proc. Phys. Soc. (London) 67B, 787 (1954).

[151] Pilling, N.B., Phys. Rev. 18, 362 (1921).

[152] Smith, J.F. and R.L. Smythe, Acta Met. 7, 261 (1959).

[153] Ruff, O. and H. Hartmann, Z. anorg. Chem. 133, 29 (1924).

[154] Rudberg, E., Phys. Rev. 46, 763 (1934).

[155] Pidgeon, L.M. and J.T.N. Atkinson, Can. Mining Met. Bull. 249, 14 (1949).

The normal boiling point of calcium was calculated to be $1765^{\circ} \pm 45^{\circ}K$, and ΔH_f° at the boiling point was taken to be 35.871 ± 0.870 Kcal/gfw.

6) Thermodynamic functions

The reference state thermodynamic functions of calcium are given in Table XIII. The ideal monatomic gas thermodynamic functions of calcium given in Table XIV were calculated using all the energy levels listed by Moore.[52] Uncertainty estimates are summarized on the back of the tables. $H^{\circ}_{298} - H^{\circ}_{0}$ was found to be 1,481 cal/mole for the ideal gas.

TABLE XIII

CALCIUM — REFERENCE STATE — Ca

Reference State for Calculating ΔH_f°, ΔF_f°, and $\log K_p$: Solid from 298.15° to 1123°K, Liquid from 1123° to 1765°K, Gas from 1765° to 6000°K.

gfw = 40.08 T_t = 737° ±10°K m.p. = 1123° ± 10°K b.p. = 1765° ±45°K

	cal/°K gfw			Kcal gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	$\log K_p$
0	0.000	0.000	Infinite	-1.375			
298.15	6.280	9.950	9.950	0.000			
300	6.287	9.989	9.950	0.012			
400	6.647	11.847	10.201	0.658			
500	7.007	13.369	10.687	1.341			
600	7.368	14.678	11.245	2.060			
700	7.729	15.841	11.820	2.815			
737	7.862	16.242	12.032	3.103			
737	7.664	16.568	12.032	3.343			
800	8.083	17.213	12.414	3.839			
900	8.775	18.205	13.003	4.682			
1000	9.490	19.166	13.571	5.595			
1100	10.221	20.105	14.123	6.580			
1123	10.390	20.318	14.248	6.817			
1123	7.400	22.161	14.248	8.887			
1200	7.400	22.652	14.771	9.457			
1300	7.400	23.244	15.400	10.197			
1400	7.400	23.792	15.980	10.937			
1500	7.400	24.303	16.518	11.677			
1600	7.400	24.781	17.020	12.417			
1700	7.400	25.229	17.490	13.157			
1765	7.400	25.504	17.777	13.638			
1765	4.980	45.827	17.777	49.509			
1800	4.982	45.927	18.325	49.683			
1900	4.993	46.197	19.785	50.182			
2000	5.008	46.453	21.112	50.682			
2100	5.030	46.698	22.325	51.184			
2200	5.061	46.933	23.438	51.689			
2300	5.101	47.158	24.464	52.197			
2400	5.153	47.377	25.415	52.709			
2500	5.219	47.588	26.297	53.228			
2600	5.300	47.794	27.120	53.753			
2700	5.397	47.996	27.889	54.288			
2800	5.511	48.194	28.611	54.833			
2900	5.644	48.390	29.290	55.391			
3000	5.796	48.584	29.930	55.963			
3100	5.968	48.777	30.535	56.551			
3200	6.160	48.969	31.107	57.157			
3300	6.371	49.162	31.652	57.783			
3400	6.601	49.355	32.169	58.432			
3500	6.849	49.550	32.663	59.104			
3600	7.115	49.747	33.135	59.802			
3700	7.397	49.946	33.587	60.528			
3800	7.692	50.147	34.020	61.282			
3900	8.001	50.351	34.436	62.067			
4000	8.320	50.557	34.836	62.883			
4100	8.648	50.767	35.223	63.731			
4200	8.983	50.979	35.595	64.613			
4300	9.323	51.194	35.955	65.528			
4400	9.666	51.413	36.305	66.477			
4500	10.010	51.634	36.643	67.461			
4600	10.353	51.858	36.971	68.479			
4700	10.694	52.084	37.290	69.532			
4800	11.030	52.313	37.601	70.618			
4900	11.362	52.543	37.903	71.737			
5000	11.687	52.776	38.198	72.890			
5100	12.004	53.011	38.487	74.075			
5200	12.313	53.247	38.768	75.290			
5300	12.612	53.484	39.043	76.537			
5400	1[illegible].902	53.723	39.313	77.813			
5500	13.181	53.962	39.577	79.117			
5600	13.450	54.202	39.836	80.448			
5700	13.708	54.442	40.090	81.806			
5800	13.954	54.683	40.340	83.190			
5900	14.190	54.923	40.585	84.597			
6000	14.414	55.164	40.826	86.027			

CALCIUM REFERENCE STATE

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	cal/°K gfw C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	Kcal/gfw $H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	± .100	±.100	±.100	±.000			
737	± .200	±.140	±.120	±.020			
737	± .300	±.230	±.120	±.080			
1123	±1.000	±.370	±.180	±.220			
1123	± .500	±.460	±.180	±.320			
1765	±1.500	±.690	±.320	±.640			
1765	± .000	±.002					
2000	± .000	±.002					
3000	± .001	±.002					
4000	± .002	±.002					
5000	± .003	±.003					
6000	± .003	±.003					

TABLE XIV

CALCIUM — IDEAL MONATOMIC GAS — Ca

Reference State for Calculating ΔH_f°, ΔF_f°, and Log K_p · Solid from 298.15° to 1123°K, Liquid from 1123° to 1765° K, Gas from 1765° to 6000°K.

gfw = 40.08 — T_t = 737° ± 10°K — m. p. = 1123° ± 10°K — b. p. = 1765° ± 45°K

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-1.481	42.114	42.114	Infinite
298.15	4.968	36.993	36.993	0.000	42.220	34.157	-25.037
300	4.968	37.024	36.993	0.009	42.217	34.107	-24.846
400	4.968	38.453	37.188	0.506	42.068	31.426	-17.170
500	4.968	39.562	37.556	1.003	41.882	28.786	-12.582
600	4.968	40.468	37.968	1.500	41.660	26.186	- 9.538
700	4.968	41.233	38.381	1.996	41.401	23.627	- 7.376
737	4.968	41.489	38.531	2.180	41.297	22.690	- 6.728
737	4.968	41.489	38.531	2.180	41.057	22.690	- 6.728
800	4.968	41.897	38.780	2.493	40.874	21.127	- 5.771
900	4.968	42.482	39.160	2.990	40.528	18.679	- 4.536
1000	4.968	43.005	39.519	3.487	40.112	16.273	- 3.556
1100	4.968	43.479	39.857	3.984	39.624	13.913	- 2.764
1123	4.968	43.582	39.933	4.098	39.501	13.376	- 2.603
1123	4.968	43.582	39.933	4.098	37.431	13.376	- 2.603
1200	4.968	43.911	40.178	4.481	37.244	11.733	- 2.137
1300	4.968	44.309	40.480	4.977	37.000	9.616	- 1.617
1400	4.969	44.677	40.767	5.474	36.757	7.518	- 1.174
1500	4.970	45.020	41.039	5.971	36.514	5.438	- 0.792
1600	4.972	45.341	41.298	6.468	36.271	3.375	- 0.461
1700	4.976	45.642	41.545	6.966	36.029	1.327	- 0.171
1765	4.980	45.827	41.696	7.289	35.871	0.000	0.000
1765	4.980	45.827	41.696	7.289			
1800	4.982	45.927	41.781	7.463			
1900	4.993	46.197	42.006	7.962			
2000	5.008	46.453	42.222	8.462			
2100	5.030	46.698	42.429	8.964			
2200	5.061	46.933	42.629	9.469			
2300	5.101	47.158	42.821	9.977			
2400	5.153	47.377	43.006	10.489			
2500	5.219	47.588	43.185	11.008			
2600	5.300	47.794	43.358	11.533			
2700	5.397	47.996	43.527	12.068			
2800	5.511	48.194	43.690	12.613			
2900	5.644	48.390	43.848	13.171			
3000	5.796	48.584	44.003	13.743			
3100	5.968	48.777	44.154	14.331			
3200	6.160	48.969	44.301	14.937			
3300	6.371	49.162	44.446	15.563			
3400	6.601	49.355	44.587	16.212			
3500	6.849	49.550	44.726	16.884			
3600	7.115	49.747	44.863	17.582			
3700	7.397	49.946	44.998	18.308			
3800	7.692	50.147	45.131	19.062			
3900	8.001	50.351	45.262	19.847			
4000	8.320	50.557	45.392	20.663			
4100	8.648	50.767	45.520	21.511			
4200	8.983	50.979	45.648	22.393			
4300	9.323	51.194	45.774	23.308			
4400	9.666	51.413	45.900	24.257			
4500	10.010	51.634	46.025	25.241			
4600	10.353	51.858	46.149	26.259			
4700	10.694	52.084	46.273	27.312			
4800	11.030	52.313	46.396	28.398			
4900	11.362	52.543	46.519	29.517			
5000	11.687	52.776	46.642	30.670			
5100	12.004	53.011	46.765	31.855			
5200	12.313	53.247	46.887	33.070			
5300	12.612	53.484	47.009	34.317			
5400	12.902	53.723	47.132	35.593			
5500	13.181	53.962	47.254	36.897			
5600	13.450	54.202	47.376	38.228			
5700	13.708	54.442	47.497	39.586			
5800	13.954	54.683	47.619	40.970			
5900	14.190	54.923	47.741	42.377			
6000	14.414	55.164	47.663	43.807			

CALCIUM IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	±.000	±.002	±.002	±.000	±.250	±.300	±.220
737	±.000	±.002	±.002	±.000	±.250	±.340	±.110
737	±.000	±.002	±.002	±.000	±.250	±.340	±.110
1123	±.000	±.002	±.002	±.000	±.450	±.450	±.088
1123	±.000	±.002	±.002	±.000	±.550	±.450	±.088
1765	±.000	±.002	±.002	±.000	±.870	±.830	±.100
1765	±.000	±.002	±.002	±.000			
2000	±.000	±.002	±.002	±.000			
3000	±.001	±.002	±.002	±.001			
4000	±.002	±.002	±.002	±.002			
5000	±.003	±.003	±.003	±.003			
6000	±.003	±.003	±.003	±.005			

4. Carbon

a. Graphite

The thermodynamic data for graphite have required extended critical review. The most recent compilations have been those of Evans[156] (up to 4000°K) and of Stull and co-workers[75] (an extension of the work of Evans up to 6000°K). The only experimental heat capacity values above 3000°K appear to be those of Rasor and McClelland.[27, 157] This work leads to values of C_p° versus T that show a very sharp rise above 3600° K and would therefore bring about marked alterations in existing thermodynamic tables for graphite if taken into account.

The rise in C_p° versus T in question is extremely rapid and its theoretical explanation appears to be uncertain. It occurs at such a high temperature that one is led to suspect insipient sublimation.

With only the available information on hand, the preparation of a reference table would be impossible at temperatures above 3600°K because C_p° (T) appears to have no finite limit.

For the above reasons, condensed phase calculations on graphite were postponed until further measurements could be made and the problem given more thought. Recent studies on this project are presented in section V-B with a detailed discussion of other available data.

b. Monatomic Gas (C)

Thermodynamic functions for the ideal monatomic gas in Table XV were calculated using the spectroscopic energy levels listed by Moore.[52] Energy levels and J values not definitely established in these tables were estimated. The calculation was carried out using the monatomic gas machine program discussed earlier in this report. Uncertainty estimates are summarized on the back of the table.

c. Diatomic Gas (C_2)

The thermodynamic properties of C_2 gas have been the subject of some disagreement for several years.[77, 158, 159] The dispute has centered about the location and number of electronic states and in particular the

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[156] National Bureau of Standards Report 6928 (1960).

[157] Rasor, N.S. and J.D. McClelland, J. Phys. Chem. Solids 15, 17 (1960).

[158] Pitzer, K.S. and E. Clementi, J. Am. Chem. Soc. 81, 4477 (1959).

[159] Altman, R.L., J. Chem. Phys. 32, 615 (1960).

characterization of the ground state. The work of Ballik and Ramsay[160, 161] is now accepted, thus firmly establishing the $^1\Sigma$ state as the ground state for the C_2 molecule. Altman[159] has recently calculated the thermodynamic functions of C_2 gas up to 5000°K based on the observed spectroscopic constants of Ballik and Ramsay.[160, 161] More recently, Clementi[162] has predicted the existence, location, and spectroscopic constants for several additional electronic states and has re-calculated the thermodynamic functions for C_2 gas from 2000° to 6000°K taking into account all experimentally observed and estimated electronic states. The thermodynamic functions of C_2 gas will be calculated using the diatomic computer program described earlier in this report with the spectroscopic data of Clementi[162] and will be reported at a later date.

d. Triatomic Gas (C_3)

Available spectroscopic constants for C_3 gas are at present estimated rather than experimentally determined values. The work of Engelke[163] offers further evidence that the $^1\Sigma$ state is the ground state of C_3 as indicated by Thorn and Winslow.[164] The fundamental frequencies were estimated by Pitzer and Clementi[158] by analogy with the allene molecule. It should be noted that the frequencies estimated by Pitzer and Clementi[158] are somewhat higher than those estimated earlier by Glockler.[165] The thermodynamic properties of C_3 in Table XVI were calculated using the linear polyatomic molecule computer program described earlier in this report with the following input data:

C-C = 1.281 Å

Moment of inertia = 65.448×10^{-40} g cm^2

Symmetry number = 2

ω_1 = 1300 cm^{-1}

ω_2 = 550 cm^{-1} (2)

ω_3 = 220 cm^{-1}

Ground electronic state = $^1\Sigma$

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[160] Ballik, E.A. and D.A. Ramsay, J. Chem. Phys. 29, 1418 (1958).

[161] Ballik, E.A. and D.A. Ramsay, J. Chem. Phys. 31, 1128 (1959).

[162] Clementi, E., Astrophys. J. 133, 303 (1961).

[163] Engelke, J., U.S. AEC Report UCRL 8727 (1959).

[164] Thorn, R.J. and G.H. Winslow, J. Chem. Phys. 26, 186 (1957).

[165] Glockler, G., J. Chem. Phys. 22, 159 (1954).

gfw = 12.011

T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal/°K gfw			Kcal/gfw			
0	0.000	0.000	Infinite				Infinite
298.15	4.981	37.761	37.761	0.000			
300	4.981	37.792	37.761	0.009			
400	4.975	39.224	37.957	0.507			
500	4.973	40.334	38.325	1.004			
600	4.971	41.240	38.738	1.502			
700	4.970	42.007	39.152	1.999			
800	4.970	42.670	39.551	2.496			
900	4.970	43.256	39.931	2.993			
1000	4.969	43.779	40.290	3.490			
1100	4.969	44.253	40.629	3.986			
1200	4.970	44.685	40.949	4.483			
1300	4.971	45.083	41.252	4.980			
1400	4.972	45.452	41.539	5.478			
1500	4.975	45.795	41.811	5.975			
1600	4.978	46.116	42.071	6.473			
1700	4.984	46.418	42.317	6.971			
1800	4.990	46.703	42.553	7.469			
1900	4.998	46.973	42.779	7.969			
2000	5.008	47.229	42.995	8.469			
2100	5.019	47.474	43.202	8.970			
2200	5.032	47.708	43.402	9.473			
2300	5.046	47.932	43.594	9.977			
2400	5.061	48.147	43.779	10.482			
2500	5.077	48.354	43.958	10.989			
2600	5.094	48.553	44.131	11.497			
2700	5.112	48.746	44.298	12.008			
2800	5.130	48.932	44.461	12.520			
2900	5.149	49.112	44.618	13.034			
3000	5.168	49.287	44.771	13.550			
3100	5.187	49.457	44.919	14.067			
3200	5.206	49.622	45.064	14.587			
3300	5.224	49.782	45.204	15.108			
3400	5.243	49.939	45.341	15.632			
3500	5.261	50.091	45.475	16.157			
3600	5.279	50.239	45.605	16.684			
3700	5.296	50.384	45.732	17.213			
3800	5.313	50.526	45.856	17.743			
3900	5.329	50.664	45.978	18.275			
4000	5.345	50.799	46.097	18.809			
4100	5.360	50.931	46.213	19.344			
4200	5.375	51.061	46.327	19.881			
4300	5.388	51.187	46.439	20.419			
4400	5.402	51.311	46.548	20.959			
4500	5.414	51.433	46.655	21.500			
4600	5.426	51.552	46.760	22.042			
4700	5.437	51.669	46.863	22.585			
4800	5.448	51.783	46.965	23.129			
4900	5.459	51.896	47.064	23.674			
5000	5.468	52.006	47.162	24.221			
5100	5.477	52.115	47.258	24.768			
5200	5.486	52.221	47.352	25.316			
5300	5.494	52.326	47.445	25.865			
5400	5.502	52.428	47.537	26.415			
5500	5.509	52.529	47.627	26.966			
5600	5.516	52.629	47.715	27.517			
5700	5.523	52.726	47.802	28.069			
5800	5.529	52.822	47.888	28.621			
5900	5.535	52.917	47.974	29.175			
6000	5.541	53.010	48.055	29.728			

CARBON IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	±.000	±.002	±.002	±.000			
1000	±.000	±.002	±.002	±.000			
2000	±.000	±.002	±.002	±.000			
3000	±.000	±.002	±.002	±.001			
4000	±.000	±.002	±.002	±.001			
5000	±.000	±.002	±.003	±.001			
6000	±.000	±.002	±.003	±.001			

The input data and calculated quantities in Table XVI are identical to those recently reported by Stull and co-workers.[75]

TABLE XVI

TRIATOMIC CARBON — IDEAL MOLECULAR GAS — C_3

gfw = 36.033

T, °K	C°_p	S°_T	$-(F^\circ_T - H^\circ_{298})/T$	$H^\circ_T - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K_p
	cal/°K gfw			Kcal/gfw			
0	0.000	0.000	Infinite				Infinite
298.15	9.388	50.689	50.689	0.000			
300	9.407	50.748	50.690	0.017			
400	10.311	53.583	51.070	1.005			
500	11.030	55.964	51.817	2.073			
600	11.623	58.029	52.684	3.207			
700	12.115	59.859	53.581	4.395			
800	12.524	61.504	54.470	5.627			
900	12.862	62.999	55.336	6.897			
1000	13.141	64.369	56.172	8.198			
1100	13.373	65.633	56.975	9.524			
1200	13.566	66.805	57.746	10.871			
1300	13.727	67.898	58.485	12.236			
1400	13.862	68.920	59.195	13.615			
1500	13.977	69.880	59.875	15.008			
1600	14.074	70.786	60.529	16.410			
1700	14.158	71.641	61.158	17.822			
1800	14.230	72.453	61.763	19.241			
1900	14.292	73.224	62.346	20.668			
2000	14.347	73.958	62.908	22.100			
2100	14.394	74.659	63.451	23.537			
2200	14.436	75.330	63.976	24.978			
2300	14.473	75.973	64.484	26.424			
2400	14.506	76.589	64.976	27.873			
2500	14.536	77.182	65.452	29.325			
2600	14.562	77.753	65.914	30.780			
2700	14.586	78.303	66.363	32.237			
2800	14.607	78.834	66.799	33.697			
2900	14.626	79.346	67.223	35.159			
3000	14.644	79.843	67.635	36.622			
3100	14.660	80.323	68.037	38.087			
3200	14.674	80.789	68.428	39.554			
3300	14.687	81.240	68.810	41.022			
3400	14.700	81.679	69.182	42.491			
3500	14.711	82.105	69.545	43.962			
3600	14.721	82.520	69.899	45.434			
3700	14.731	82.923	70.246	46.906			
3800	14.739	83.316	70.585	48.380			
3900	14.748	83.699	70.916	49.854			
4000	14.755	84.073	71.241	51.329			
4100	14.762	84.437	71.558	52.805			
4200	14.769	84.793	71.869	54.282			
4300	14.775	85.141	72.173	55.759			
4400	14.781	85.480	72.472	57.237			
4500	14.786	85.813	72.765	58.715			
4600	14.791	86.138	73.052	60.194			
4700	14.796	86.456	73.334	61.673			
4800	14.800	86.767	73.610	63.153			
4900	14.804	87.073	73.882	64.633			
5000	14.808	87.372	74.149	66.114			
5100	14.812	87.665	74.411	67.595			
5200	14.815	87.953	74.669	69.076			
5300	14.819	88.235	74.922	70.558			
5400	14.822	88.512	75.171	72.040			
5500	14.825	88.784	75.416	73.522			
5600	14.827	89.051	75.657	75.005			
5700	14.830	89.313	75.895	76.488			
5800	14.833	89.571	76.128	77.971			
5900	14.835	89.825	76.358	79.454			
6000	14.837	90.075	76.585	80.938			

5. Chromium

a. Solid-State Transitions of Chromium

The stable form of solid chromium at 25°C is the body-centered cubic crystal.[166-168] A transition, believed to be antiferromagnetic, occurs at 38.5° ± 0.3°C. A second solid-state transition, of unknown type, occurs at 1375° ± 25°C. The transition from body-centered cubic to face-centered cubic occurs at 1815° ± 30°C. The melting point of chromium is 1875° ± 30°C, and the estimated standard boiling point is 2649° ± 200°C. These transitions and their accompanying heat effects are listed in Table XVII.

1) The 38.5°C transition

Abnormalities in several properties near 40°C were observed by a number of workers,[169] but only recently was an anomaly in the heat capacity experimentally observed.[170] The shape and position of the heat-capacity anomaly were consistent with those of an antiferromagnetic transition. The transition was observed to occur at 38.5° ± 0.3°C with ΔH_t equal to 1.4 cal/g atom and ΔS_t equal to 0.0044 e.u./g atom.

TABLE XVII

TRANSITION DATA FOR CHROMIUM

Transition	Temperature (°K)	ΔH_t(cal/g atom)
Solid I $\longrightarrow$ Solid II	311.65 ± 0.3	1.4
Solid II $\longrightarrow$ Solid III	1648 ± 25	800 ± 200
Solid III $\longrightarrow$ Solid IV	2088 ± 30	350 ± 100
Solid IV $\longrightarrow$ Liquid	2148 ± 30	4920 ± 1000
Liquid $\longrightarrow$ Gas	2967 ± 200	80, 220 ± 3150
Solid I $\longrightarrow$ Gas	298.15	94, 820 ± 500

[166] Fine, M.E., E.S. Greiner, and W.C. Ellis, J. Metals 191, 56 (1951).

[167] Sully, A.H., E.A. Brandes, and K.W. Mitchell, J. Inst. Met. 81, 585 (1953).

[168] Pearson, W.B. and W. Hume-Rothery, J. Inst. Met. 81, 311 (1953).

[169] Sully, A.H., Chromium, Butterworths, London (1954).

[170] Beaumont, R.H., H.Chikera, and J.A. Morrison, Phil. Mag. 5, 188 (1960).

2) The 1375°C transition

The existence of a transition [Cr(II) ⟶ Cr(III)] at about 1400°C was indicated by the observation of an anomaly in magnetic susceptibility.[171] More conclusive evidence was provided by heat capacity measurements recently reported by Krauss.[172] The latter measurements showed a maximum in the heat capacity versus temperature curve at about 1375°C. Approximate graphical integration of the area under the observed heat capacity curve has yielded a heat of transition(ΔH_t) value of 800 ± 200 cal/g atom. A comparison of Lucks[173] enthalpies measured by the drop method in this temperature range and enthalpies estimated (assuming the nonexistence of any transition) by Kelley[56] has led to an estimated ΔH_t of about 800 cal/g atom. It should be noted that evidence for the existence of this transition was not observed by McCaldin and Duwez[174] in a thermal analysis study.

3) The body-centered cubic to face-centered cubic transition

The existence of the Cr(III) ⟶ Cr (IV) transformation was established by cooling-curve analysis.[175] The crystal structure of the new phase was studied by Abrahamson and Grant.[176] The temperature of the transition was reported to be 1840° ± 15°C,[175] but was herein revised downward since the melting point reported in the same paper was probably high. The difference between the melting-point and transition temperatures was not altered in doing this. Heat capacities have not been measured in the vicinity of this transition, and no experimental value for ΔH_t was available. The estimate of Stull and Sinke;[77] i.e., ΔH_t = 350 cal/g atom, was accepted. The uncertainty in this value was estimated to be ± 100 cal/g atom. Again, the existence of a transition at this temperature was not observed by McCaldin and Duwez.[174]

4) The melting point of chromium

Values of the melting point of chromium reported in the literature ranged from 1515° to 1903°C.[169] Even recent measurements using very pure chromium showed a considerable spread. The "best" values were the following:

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[171] McGuire, T.R. and C.J. Kriessman, Phys. Rev. 85, 452 (1952).

[172] Krauss, F., Z. Metalik 49, 386 (1958).

[173] Lucks, C.F. and H.W. Deem, WADC Tech. Rept 55-496 (November 1955).

[174] McCaldin, J.O. and F. Duwez, J. Metals 6; AIME Trans. 200, 619 (1954).

[175] Bloom, D.S., J.W. Putman, and N.J. Grant, J. Metals 4, 626 (1952).

[176] Abrahamson, E.P. and N.J. Grant, J. Metals 8; AIME Trans. 206, 975 (1956).

1890 ± 10°C,[177]

1860 ± 10°C,[178]

1845 ± 10°C,[179]

1903 ± 10°C,[175]

1875 ± 5°C.[180]

An average of these values was chosen as the most probable melting point, i.e., 1875° ± 30°C. The uncertainty was picked to include all the above values.

The heat of fusion at the melting point has also not been unambiguously established. Measured and estimated values reported include the following:

3650 cal/g atom,[181]

4200 cal/g atom,[26]

3300 cal/g atom,[77]

4600 cal/g atom,[182]

5000 cal/g atom.[56, 76]

In the absence of conclusive experimental data, an estimated heat of fusion of 4920 cal/g atom was calculated from an assumed entropy of fusion of 2.3 e.u./g atom.

In view of the wide range of reported values, an uncertainty of ± 1000 cal/g atom was assigned to the heat of fusion at the melting point.

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[177] Graube, H. and R. Knabe, Z. Elektrochem. 42, 793 (1936).

[178] Carlile, S.J., J.W. Christian, and W. Hume-Rothery, J. Inst. Met. 16, 169 (1949).

[179] Greenaway, H.T., S.T.M. Johnstone, and M.K. McQuillan, J. Inst. Met. 19, 109 (1951).

[180] Wyman, L.L. and J.T. Sterling, Ductile Chromium and Its Alloys, American Society for Metals, Cleveland (1957), p. 180.

[181] Umino, S., Sci. Repts. Tohoku Imp. Univ. First Series 15, 597 (1926).

[182] Kubaschewski, O. and E. Evans, Metallurgical Thermochemistry, Pergamon Press, N.Y. (1958).

5) The standard heat of sublimation at 298.15°K (ΔH°_{s298})

Vapor pressure measurements for solid chromium have been reported by several workers during the past decade.[183-189] The first four papers contained experimental vapor pressure values, whereas only vapor pressure equations were available from the other papers. ΔH°_{s298} values, calculated using reported vapor pressure values and free-energy functions from the present compilation, were as follows:

94,710 cal/g atom,[183]

95,250 cal/g atom,[184]

94,870 cal/g atom,[185]

94,750 cal/g atom,[187]

94,530 cal/g atom.[188]

An average value of ΔH°_{s298} = 94,820 ± 500 cal/g atom was chosen. The vapor pressure measurements of Nesmeyanov and Man,[186] and of Burlakov,[189] lead to appreciably lower ΔH°_{s298} values, and were not included.

6) The boiling point of chromium

A value of 2200°C was reported by Greenwood[190] for the boiling point of Cr, but it was considered to be low by later workers.[77, 191] Baur and Brunner[92] have calculated a value of 2660°C from vapor pressure measurements. Later workers[76, 77] have estimated the boiling point from calculated values of ΔH°_{v0} or ΔH°_{v298} and free-energy functions for the gas and the condensed phase (i.e., the standard boiling temperature was taken as the temperature at which ΔF becomes zero for the change from condensed phase to gaseous phase).

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[183]Speiser, R., H.L. Johnston and P. Blackburn, J. Am. Chem. Soc. 72, 4142 (1950).

[184]Gulbransen, E.A. and K.F. Andrew, J. Electrochem. Soc. 99, 402 (1952).

[185]McCabe, C.L., R.G. Hudson, and H.W. Paxton, Trans. Am. Inst. Mining. Met. Petrol. Engrs. 212, 102 (1958).

[186]Nesmeyanov, A. and D. Man. Proc. Acad. Sci. (U.S.S.R.), Phys. Chem. Sec.(English Transl.) 131, 373 (1960).

[187]Kubaschewski, O. and G. Heymer, Acta. Met. 8, 416 (1960).

[188]Vintaiker, E.Z. Proc. Acad. Sci. (U.S.S.R.), Phys. Chem. Sec. (English Transl.) 129, 951 (1959).

[189]Burlakov, V.D., Fiz. Metal. i. Metalloved. 5, 91 (1957).

[190]Greenwood, H.C., Proc. Roy. Soc. A82, 396 (1905).

[191]Kelley, K.K., U.S. Bur. Mines Bull. 383 (1935).

Stull and Sinke[77] thus calculated a value of 2642°C, and Hultgren[76] calculated a value of 2665°C. For the present compilation, a boiling point of 2694° ± 200°C was adopted. The ΔH of vaporization could then be estimated from the value of ΔH°_{298} and the enthalpy functions for the two phases at the standard boiling point. A value of ΔH of vaporization at the standard boiling point of 80, 220 ± 3150 cal/g atom was thus calculated in the present work.

b. Thermodynamic Functions for the Condensed Phases of Chromium

Recent compilations of the thermodynamic functions of solid and liquid chromium included those of Stull and Sinke,[77] Hultgren,[76] and Kelley.[56] Stull and Sinke used a rather low value for the ΔH of fusion and did not include the solid-solid transformations at 38.5° and 1375°C. The other two compilations did not include the solid-solid transformations at 38.5°, 1375°, and 1815°C. The values of enthalpy and entropy at 298.15°K listed by Hultgren were accepted in the present work.

$H^\circ_{298} - H^\circ_0 = 970$ cal/g atom,

$S^\circ_{298} = 5.68$ e.u./g atom.

The enthalpy functions for solid chromium (i.e., $H^\circ_T - H^\circ_{298}$) in Table XVIII were those of Kelley,[56] corrected to include the various transitions given in Table XVII. The tabular entropy values for solid chromium were calculated by the method of Kelley.[56] Uncertainty estimates are are summarized on the back of Table XVIII.

Values for the $-\left(\dfrac{F^\circ_T - H^\circ_{298}}{T}\right)$ function of solid chromium were calculated from equation (108).

Heat capacity values for solid chromium were not well established (see section IV-A5d below), and very limited data were available near the various transitions.[170, 172] Tabular values of C°_p for solid chromium were therefore calculated from Kelley's equation.[56] These calculated values represented experimental values fairly accurately except in transition regions where experimental data were nonexistent or insufficient for complete evaluation.

The value of the heat capacity of liquid chromium was taken to be constant at 9.40 cal/°K g atom[56, 76] even though the only experimental determination of C°_p on liquid chromium yielded a value of 9.7 cal/°K g atom,[181] because the chromium used in this single experimental determination must be considered to have been impure since the observed melting point was about 350°C lower than the "true" value. Entropy values for liquid chromium were calculated, using the value of 9.40 cal/°K g atom for C_p^o, according to the equation

$$S_T^o = C_p^o \ln T + C_1 \quad . \tag{138}$$

$H_T^o - H_{298}^o$ values for liquid chromium were calculated from the equation

$$H_T^o - H_{298}^o = C_p^o T + C_2 \quad . \tag{139}$$

The values of the constants, C_1 and C_2, in the above equations were evaluated from the tabular values of S_T^o and $H_T^o - H_{298}^o$ for liquid chromium at the melting point. The free-energy function for liquid chromium was evaluated in the same manner as that used for solid chromium.

c. Thermodynamic Functions for Gaseous Chromium

Thermodynamic properties for the ideal monatomic gas given in Table XIX were calculated using the spectroscopic energy levels listed by Moore.[52] Energy levels and values not definitely established in these tables were estimated. The equations employed in these calculations have been summarized in two recent publications[51, 75] (see Sect. III-D). Uncertainty estimates are summarized on the back of Table XIX. $H_{298}^o - H_0^o$ was found to be 1,481 cal/mole.

ΔH_f^o, ΔF_f^o, and $\text{Log}_{10} K_p$ for gaseous chromium were calculated by means of the equations in section III-D1g.

d. Uncertainties in Condensed Phase Functions

The available basic data for chromium included both heat capacity[170, 172, 192, 193] and enthalpy[173, 181, 194, 195] values. The error analysis used was based on the uncertainty of the C_p^o data, as explained in section III-G1d.

1) Heat capacity

Sully[169] has critically reviewed reported C_p values near room temperature and concluded that their accuracy was about ± 3 percent. A graphical comparison in this work also led to about the same uncertainty. The uncertainty in C_p at 298.15°K was thus

[192] Anderson, C.T., J. Am. Chem. Soc. 59, 488 (1937).

[193] Armstrong, L.D. and H. Grayson-Smith, Can. J. Phys. 28A, 51 (1950).

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TABLE XVIII

CHROMIUM — REFERENCE STATE — Cr

Reference State for Calculating ΔH_f°, ΔF_f°, and $\text{Log}\, K_p$: Solid from 298.15° to 2148°K, Liquid from 2148° to 2967°K, Gas from 2967° to 6000°K.

gfw = 52.01 T_t(I) = 311.65°±0.3°K T_t(II) = 1648°±25°K T_t(III) = 2088°±30°K m.p. = 2148°±30°K b.p. = 2967°±200°K

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-0.970			
298.15	5.577	5.680	5.680	0.000			
300	5.579	5.714	5.681	0.010			
311.65	5.597	5.934	5.687	0.077			
311.65	5.597	5.938	5.687	0.078			
400	5.800	7.400	5.913	0.595			
500	6.090	8.794	6.354	1.220			
600	6.415	9.978	6.861	1.870			
700	6.755	10.995	7.380	2.530			
800	7.103	11.902	7.890	3.210			
900	7.455	12.726	8.382	3.910			
1000	7.810	13.495	8.855	4.640			
1100	8.167	14.229	9.310	5.410			
1200	8.525	14.942	9.750	6.230			
1300	8.884	15.638	10.177	7.100			
1400	9.243	16.312	10.591	8.010			
1500	9.603	16.961	10.994	8.950			
1600	9.964	17.587	11.387	9.920			
1648	10.137	17.882	11.571	10.400			
1648	10.137	18.368	11.571	11.200			
1700	10.324	18.684	11.784	11.730			
1800	10.685	19.284	12.184	12.780			
1900	11.046	19.879	12.573	13.880			
2000	11.408	20.463	12.953	15.020			
2088	11.726	20.975	13.281	16.065			
2088	11.726	21.142	13.281	16.415			
2100	11.769	21.212	13.327	16.560			
2148	11.942	21.486	13.517	17.117			
2148	9.400	23.786	13.517	22.057			
2200	9.400	24.011	13.763	22.545			
2300	9.400	24.429	14.218	23.485			
2400	9.400	24.829	14.652	24.425			
2500	9.400	25.213	15.067	25.365			
2600	9.400	25.581	15.464	26.305			
2700	9.400	25.936	15.845	27.245			
2800	9.400	26.278	16.212	28.185			
2900	9.400	26.608	16.565	29.125			
2967	9.400	26.822	16.794	29.755			
2967	7.317	53.861	16.794	109.974			
3000	7.359	53.943	17.204	110.216			
3100	7.481	54.186	18.393	110.958			
3200	7.599	54.425	19.515	111.712			
3300	7.713	54.661	20.577	112.478			
3400	7.825	54.893	21.583	113.255			
3500	7.935	55.121	22.537	114.043			
3600	8.045	55.346	23.445	114.842			
3700	8.157	55.568	24.311	115.652			
3800	8.270	55.787	25.136	116.473			
3900	8.386	56.004	25.926	117.306			
4000	8.506	56.217	26.679	118.151			
4100	8.631	56.429	27.402	119.008			
4200	8.761	56.638	28.096	119.877			
4300	8.896	56.846	28.762	120.760			
4400	9.036	57.052	29.403	121.657			
4500	9.183	57.257	30.020	122.567			
4600	9.335	57.460	30.614	123.493			
4700	9.492	57.663	31.187	124.435			
4800	9.654	57.864	31.741	125.392			
4900	9.821	58.065	32.276	126.366			
5000	9.992	58.265	32.794	127.356			
5100	10.167	58.465	33.296	128.364			
5200	10.344	58.664	33.781	129.390			
5300	10.524	58.863	34.253	130.433			
5400	10.705	59.061	34.710	131.495			
5500	10.887	59.259	35.155	132.574			
5600	11.069	59.457	35.587	133.672			
5700	11.250	59.655	36.008	134.788			
5800	11.429	59.852	36.417	135.922			
5900	11.605	60.049	36.816	137.074			
6000	11.779	60.245	37.204	138.243			

CHROMIUM REFERENCE STATE

SUMMARY OF UNCERTAINTY ESTIMATES

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	± .200	± .070	± .070	± .000			
311.65	± .200	± .080	± .070	± .003			
311.65	± .200	± .080	± .070	± .003			
1000	± .700	± .600	± .290	± .310			
1648	±1.200	±1.070	± .510	± .930			
1648	±1.200	±1.190	± .510	±1.130			
2000	±1.200	±1.420	± .640	±1.550			
2088	±1.200	±1.470	± .680	±1.660			
2088	±1.200	±1.520	± .680	±1.760			
2184	±1.200	±1.550	± .700	±1.830			
2184	±1.000	±2.020	± .700	±2.830			
2967	±1.000	±2.340	±1.450	±2.650			
2967	± .000	± .003					
3000	± .001						
4000	± .001	± .003					
5000	± .002	± .003					
6000	± .002	± .003					

TABLE XIX

CHROMIUM — IDEAL MONATOMIC GAS — Cr

Reference State for Calculating ΔH_f°, ΔF_f°, and $\log K_p$: Solid from 298.15° to 2148°K, Liquid from 2148° to 2967°K, Gas from 2967° to 6000°K.

gfw = 52.01 T_t(I) = 311.65°±0.3°K T_t(II) = 1648°±25°K T_t(III) = 2088°±30°K m.p. = 2148°±30°K b.p. = 2967°±200°K

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	$\log K_p$
0	0.000	0.000	Infinite	-1.481	94.309	94.309	Infinite
298.15	4.968	41.637	41.637	0.000	94.820	84.099	-61.644
300	4.968	41.668	41.637	0.009	94.819	84.033	-61.215
311.65	4.968	41.857	41.642	0.067	94.810	83.615	-58.633
311.65	4.968	41.857	41.642	0.067	94.809	83.615	-58.633
400	4.968	43.097	41.832	0.506	94.731	80.452	-43.955
500	4.968	44.206	42.200	1.003	94.603	76.897	-33.610
600	4.968	45.111	42.612	1.500	94.450	73.369	-26.723
700	4.968	45.877	43.025	1.996	94.286	69.868	-21.813
800	4.969	46.541	43.424	2.493	94.103	66.393	-18.137
900	4.972	47.126	43.803	2.990	93.900	62.942	-15.284
1000	4.980	47.650	44.162	3.488	93.668	59.513	-13.006
1100	4.996	48.126	44.501	3.987	93.397	56.109	-11.147
1200	5.023	48.561	44.822	4.487	93.077	52.734	-9.604
1300	5.065	48.965	45.125	4.992	92.712	49.387	-8.302
1400	5.125	49.342	45.413	5.501	92.311	46.070	-7.191
1500	5.203	49.698	45.687	6.017	91.887	42.780	-6.233
1600	5.300	50.037	45.948	6.542	91.442	39.523	-5.398
1648	5.353	50.195	46.070	6.798	91.218	37.965	-5.034
1648	5.353	50.195	46.070	6.798	90.418	37.965	-5.034
1700	5.414	50.362	46.199	7.078	90.168	36.314	-4.668
1800	5.545	50.675	46.439	7.626	89.666	33.161	-4.026
1900	5.688	50.979	46.670	8.187	89.127	30.035	-3.455
2000	5.841	51.274	46.892	8.763	88.563	26.222	-2.865
2088	5.982	51.529	47.082	9.284	88.039	24.244	-2.537
2088	5.982	51.529	47.082	9.284	87.689	24.244	-2.537
2100	6.001	51.563	47.108	9.356	87.616	23.879	-2.485
2148	6.080	51.700	47.209	9.646	87.349	22.449	-2.284
2148	6.080	51.700	47.209	9.646	82.409	22.449	-2.284
2200	6.165	51.846	47.317	9.964	82.239	21.001	-2.086
2300	6.330	52.124	47.520	10.589	81.924	18.225	-1.732
2400	6.493	52.397	47.717	11.230	81.625	15.463	-1.408
2500	6.652	52.665	47.910	11.887	81.342	12.713	-1.111
2600	6.806	52.929	48.098	12.560	81.075	9.971	-0.838
2700	6.954	53.188	48.282	13.248	80.823	7.241	-0.586
2800	7.095	53.444	48.462	13.951	80.586	4.519	-0.353
2900	7.230	53.695	48.638	14.667	80.362	1.810	-0.136
2967	7.317	53.861	48.754	15.154	80.219	0.000	0.000
2967	7.317	53.861	48.754	15.154			
3000	7.359	53.943	48.810	15.396			
3100	7.481	54.186	48.980	16.138			
3200	7.599	54.425	49.146	16.892			
3300	7.713	54.661	49.310	17.658			
3400	7.825	54.893	49.471	18.435			
3500	7.935	55.121	49.629	19.223			
3600	8.045	55.346	49.785	20.022			
3700	8.157	55.568	49.938	20.832			
3800	8.270	55.787	50.089	21.653			
3900	8.386	56.004	50.238	22.486			
4000	8.506	56.217	50.385	23.331			
4100	8.631	56.429	50.529	24.188			
4200	8.761	56.638	50.672	25.057			
4300	8.896	56.846	50.814	25.940			
4400	9.036	57.052	50.953	26.837			
4500	9.183	57.257	51.091	27.747			
4600	9.335	57.460	51.227	28.673			
4700	9.492	57.663	51.362	29.615			
4800	9.654	57.864	51.495	30.572			
4900	9.821	58.065	51.627	31.546			
5000	9.992	58.265	51.758	32.536			
5100	10.167	58.465	51.888	33.544			
5200	10.344	58.664	52.016	34.570			
5300	10.524	58.863	52.143	35.613			
5400	10.705	59.061	52.270	36.675			
5500	10.887	59.259	52.395	37.754			
5600	11.069	59.457	52.519	38.852			
5700	11.250	59.655	52.643	39.968			
5800	11.429	59.852	52.765	41.102			
5900	11.605	60.049	52.887	42.254			
6000	11.779	60.245	53.008	43.423			

CHROMIUM IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	±.000	±.002	±.002	±.000	± .500	± .520	±.380
311.65	±.000	±.002	±.002	±.000	± .500	± .520	±.360
311.65	±.000	±.002	±.002	±.000	± .500	± .520	±.360
1000	±.000	±.002	±.002	±.000	± .810	± .790	±.170
1648	±.000	±.002	±.002	±.000	±1.430	±1.340	±.180
1648	±.000	±.002	±.002	±.000	±1.630	±1.340	±.180
2000	±.001	±.002	±.003	±.000	±2.050	±1.790	±.200
2088	±.001	±.002	±.003	±.000	±2.160	±1.930	±.200
2088	±.001	±.002	±.003	±.000	±2.260	±1.930	±.200
2148	±.001	±.002	±.003	±.001	±2.330	±2.010	±.200
2148	±.001	±.002	±.003	±.001	±3.330	±2.010	±.200
2967	±.001	±.003	±.003	±.001	±3.150	±4.810	±.350
2967	±.001	±.003	±.003	±.001			
3000	±.001	±.003	±.003	±.001			
4000	±.001	±.003	±.003	±.002			
5000	±.002	±.003	±.003	±.003			
6000	±.002	±.003	±.003	±.005			

taken to be ± 0.2 cal/°K g atom. The uncertainty was taken to be the same at the first transition point of 311.65°K. An uncertainty of ± 0.7 cal/°K g atom was estimated from a comparison of reported values near 1000°K.[172, 173, 181, 193, 195] The uncertainty at the 1648°K transition point was difficult to assign since direct C_p° values have been reported in only one paper,[172] and other workers[173, 181, 194] have measured enthalpies which included or partially included the heat of transition. The uncertainty was therefore increased to ± 1.2 cal/°K g atom at 1648°K.

The only measurements above 1800°K were those of Umino[181] made on impure chromium. In the absence of experimental C_p° values, the uncertainties at 2000°, 2088°, and 2148°K were assumed to be the same as the uncertainty at 1648°K; i.e., ±1.2 cal/°K g atom. As stated earlier, the C_p° of liquid chromium was measured by only one worker[181] using impure chromium; an uncertainty of ± 1.0 cal/°K g atom was therefore arbitrarily assigned over the whole liquid range.

2) Entropy

Uncertainties in entropy values were calculated from assigned uncertainties in C_p° values and heats of transition as explained in Section IV-Gld. The uncertainty in S_{298}° was taken to be ±0.07 e.u./g atom after Kelley.[139]

3) Enthalpy

Uncertainties in enthalpy values were calculated from C_p° uncertainties and assigned values of ΔH-of-transition uncertainties as explained in section III-Gld. The equations used for single-phase regions and transitions were as follows:

$$h_{T_2} = h_{T_1} + \delta C_p^\circ (T_2 - T_1) , \tag{140}$$

$$h_B = h_A + \delta \Delta H_t . \tag{141}$$

4) Free energy

The uncertainty in the free-energy function was calculated from calculated uncertainties in S_T° and $H_T^\circ - H_{298}^\circ$ using equations (119) and (120).

e. Uncertainties in Gas-Phase Functions

Uncertainty estimates for the calculated thermodynamic functions of the ideal monatomic gas were made with the machine program described in section III and are summarized on the back of Table XIY.

f. Other References Pertaining to the Thermodynamics of Chromium

Sully[169] has reviewed other heat capacity measurements not previously mentioned in the present discussion. His review included the work of Dewar,[196] Richards and Jackson,[197] Nordmeyer and Bernoulli,[198] Lammel,[199] Schimpff,[200] Schubel,[201] and Mache.[202]

Heat capacity measurements at very low temperatures (below 20°K) have been reported and discussed by Rayne and Kemp,[203] Wolcott,[204] Friedberg, Estermann, and Goldman,[205] and Estermann, Friedberg, and Goldman.[206]

Transitions in solid chromium have been reviewed by Sully,[169] and discussed more recently by Pursey[207] and by Beaumont and co-workers.[170] The possible existence of a hexagonal modification of chromium has been discussed by Sully,[169] and in more recent papers; e.g., Brummer and Suwalski.[208]

A useful annotated bibliography of thermal properties of chromium was that of Goodwin.[209] A recent review of the properties of high-purity chromium was that of Edwards, Nish, and Wain.[210]

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[196] Dewar, J., Proc. Roy. Soc. A89, 158 (1913).

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[202] Mache, H., Akad. Wiss. Wien 106, 590 (1897).

[203] Rayne, J.A. and W.R. G. Kemp, Phil. Mag. 1, 918 (1956).

[204] Wolcott, N.M., Bull. Inst. Intern. Froid Annexe (1955), p. 286.

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[206] Estermann, I., S.A. Friedberg, and J.E. Goldman, Phys. Rev. 87, 582 (1952).

[207] Pursey, H., J. Inst. Met. 86, 362 (1958).

[208] Brummer O. and Suwalski, G. Naturwissenschaften 46, 223 (1959).

[209] Goodwin, T.C. and M.W. Ayton, WADC TR-56-423, AD-111-846 (August 1956).

[210] Edwards, A.R., J.I. Nish, and H.L. Wain, Met. Revs. 4, 403 (1959).

6. Hafnium

a. Selection of Condensed Phase Data

1) Crystal structure and solid-state transition

Hafnium exists in two known crystalline modifications.[211] The ordinary room-temperature form has a hexagonal, close-packed structure, while the high temperature form has a body-centered cubic structure.

The transition temperature for equilibrium between the two crystalline modifications was taken to be 2033° ± 35° K, as found by Deardorff and Kato,[212] and accepted by Thomas and Hayes.[211] Other reported values mentioned by Hansen[213] are as follows:

Temp. (° K)	Source
1603-1903	Zwikker[214]
1583	Duwez[215]
2223 ± 100	Fast[216]
1973	Hansen and Anderko[213]

It is noteworthy that the value chosen by Hansen and Anderko[213] does not differ markedly from the one chosen here which is based on newer data.

2) Melting point

A temperature of 2495° ± 30° K was accepted as the melting point for hafnium metal. This value is based on the work of Deardorff and Hayes,[217] and has been accepted by Thomas and Hayes.[211] Earlier data have been reviewed by Stull and Sinke[77] who chose a value of 2250° K. The more recent value recommended herein appears to be preferable.

[211] Thomas, D.E. and E.T. Hayes, The Metallurgy of Hafnium, U.S. AEC (1960).

[212] Deardorff, D.K. and H. Kato, The Transformation Temperature of Hafnium, USBM-U-426 (8 April 1958).

[213] Hansen, M. and K. Anderko, Constitution of Binary Alloys, McGraw-Hill, N.Y. (1958).

[214] Zwikker, C., Physica 6, 361 (1936).

[215] Duwez, P., J. Appl. Phys. 22, 1174 (1951).

[216] Fast, J.D., J. Appl. Phys. 23, 350 (1952).

[217] Deardorff, D.K. and E.T. Hayes, Melting point determinations of hafnium metal, Trans. AIME 206, 509 (1956).

3) Heat of transition

No experimental data were available for the heat of transition of Hf. Stull and Sinke[77] combined the heats of transition and melting into a single quantity. For the present case, it was calculated from an entropy of transition estimated from those of titanium and zirconium (i.e., 0.822 and 0.806 e.u., respectively). The intermediate value of 0.811 e.u. was chosen for Hf, resulting in a heat of transition of 1650 ± 200 cal/mole at 2033° K.

4) Heat of fusion

The heat of fusion of Hf also had to be estimated. For titanium, the entropy of fusion was taken to be 2.10 e.u. This same value was used for Hf along with a melting point of 2495° K to give a ΔH_{fusion} value of 5239 ± 1000 cal/mole. This value of the heat of fusion agrees well (probably fortuitously) with that of Stull and Sinke,[77] who included the heat change associated with the transition to obtain a contribution of ΔH_{fusion} = 5200 cal/g atom.

5) Low-temperature heat capacity and S°_{298}

Heat capacity data for the temperature range from 10° to 200° K have been reported by Burk et al.[218] For the range from 25° to 100° C, Adenstedt[219] has reported an average value of $\overline{C^\circ_p}$ = 6.27 cal/° K g atom. From the rate of change of C°_p with temperature given by Stull and Sinke,[77] values of $C^\circ_{p,\ 298^\circ K}$ = 6.225 cal/° K g atom, $C^\circ_{p,\ 375^\circ K}$ = 6.315 cal/° K g atom, and $C^\circ_{p,\ 400^\circ K}$ = 6.345 cal/° K g atom were calculated with Adenstedt's[219] data. These values have been used with the data of Burk et al[218] to determine that $H^\circ_{298} - H^\circ_0$ = 1.428 Kcal/g atom and S°_{298} = 10.666 e.u. This value of $H^\circ_{298} - H^\circ_0$, obtained by graphical integration, agreed well with a trapezoidal rule integration value of 1.429 Kcal/g atom. The entropy value was obtained by graphical integration of C°_p/T versus T data. The values of $H^\circ_{298} - H^\circ_0$, and S°_{298} found by Stull and Sinke[77] were 1.448 Kcal/g atom and 10.91 e.u. respectively.

6) High-temperature heat capacity

Experimental heat capacity data for elemental hafnium at elevated temperatures were not available. Accordingly, values were

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[218] Burk, D.L., I. Estermann, and S. Friedberg, Z. physik. chem. Neue Folge 16, 183 (1958).

[219] Adenstedt, H.K., Trans ASM 44, 949 (1952).

estimated with the help of data on titanium and zirconium. C_p° data given by Kelley[56] for zirconium and titanium were plotted against temperatures with the hafnium data from Stull and Sinke.[77] The final choice was a set of data intermediate between the Ti, Zr, and Hf data. This corresponded to a line parallel to and about 0.18 cal/° K g atom above the Stull and Sinke data, but joining smoothly with the low temperature data discussed in Section IV-A6 above.

7) Heat of vaporization

Direct experimental values for the heat of vaporization were not known. However, Lewis and Randall[220] have tabulated a value of 168 ± 10 Kcal/g atom. This value is the one used by Stull and Sinke[77] and was accepted here.

8) The liquid heat capacity

For temperatures above the accepted melting point, the liquid heat capacity was estimated to be 8.0 cal/° K g atom. This is the value used by Stull and Sinke.[77]

9) Calculation of the reference-state table

The data used in the reference-state calculations for Table XXI are given in Table XX which provides a convenient summary of the "best" property values. Uncertainty estimates are summarized on the back of Table XXI.

b. Selection of Data for the Ideal Monatomic Gas

The energy levels given by Moore,[221] based on the work of Meggers,[222] were used to calculate the values of the ideal monatomic gas thermodynamic functions in Table XXII.

The values in Table XXII should be regarded as tentative, even though they supersede those of Stull and Sinke,[77] because Meggers[223] has found 29 new even and 32 odd levels since his earlier work.[221,222] The table will be brought up to date as soon as Megger's new energy levels become available. The val of $H_{298}^\circ - H_0^\circ$ was found to be 1,481 cal/mole. Error estimates are summarized on the back of the table.

[220] Lewis, G.N., M. Randall, K. Pitzer and L. Brewer, Thermodynamics, 2nd ed. Mc Graw-Hill, N.Y. (1961).

[221] Moore, C., Nat. Bur. Stds. Circ. 467, vol. 3 (1 May 1958).

[222] Meggers, W.F., J. Research Nat. Bur. Stds. 61, 269 (1958).

[223] Meggers, W.F., Private Communication (7 April 1961).

TABLE XX

SUMMARY OF HAFNIUM DATA

Quantity	Units	Value
T_t (transition temp.)	°K	2033 ± 35
ΔH_t (heat of transition)	Kcal/gfw	1.650 ± 0.200
Melting point	°K	2495 ± 30
ΔH_m (heat of fusion)	Kcal/gfw	5.239 ± 1.000
S°_{298} (solid)	e.u.	10.666 ± 0.10
ΔH_v	Kcal/gfw	159.248
T_b (boiling point)	°K	5536.37
$\Delta H^\circ_{s\ 298}$	Kcal/gfw	168.000 ± 10.000
$H^\circ_{298} - H^\circ_0$ (solid)	Kcal/gfw	1.428 ± 0.010

TABLE XXI

HAFNIUM — REFERENCE STATE — Hf

Reference State for Calculating ΔH_f°, ΔF_f°, and $\text{Log } K_p$: Solid from 298.15° to 2495°K, Liquid from 2495° to 5536°K, Gas from 5536° to 6000°K.

gfw = 178.50 $\quad$ T_t(I) = 2033° ± 200°K $\quad$ m.p. = 2495° ± 30°K $\quad$ b.p. = 5536° ± 600°K*

T, °K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal/gfw)	ΔH_f° (Kcal/gfw)	ΔF_f° (Kcal/gfw)	Log K_p
0	0.000	0.000	Infinite	-1.428			
298.15	6.225	10.666	10.666	0.000			
300	6.226	10.705	10.666	0.012			
400	6.345	12.504	10.907	0.639			
500	6.466	13.936	11.377	1.280			
600	6.583	15.127	11.906	1.932			
700	6.701	16.151	12.442	2.596			
800	6.815	17.054	12.963	3.272			
900	6.925	17.863	13.464	3.959			
1000	7.045	18.599	13.941	4.658			
1100	7.164	19.276	14.396	5.368			
1200	7.284	19.904	14.829	6.090			
1300	7.399	20.492	15.242	6.825			
1400	7.518	21.045	15.637	7.570			
1500	7.640	21.568	16.015	8.328			
1600	7.765	22.065	16.378	9.099			
1700	7.885	22.539	16.727	9.881			
1800	8.005	22.993	17.062	10.676			
1900	8.126	23.429	17.386	11.482			
2000	8.248	23.849	17.699	12.301			
2033	8.288	23.984	17.800	12.574			
2033	8.295	24.796	17.800	14.224			
2100	8.378	25.066	18.027	14.782			
2200	8.501	25.459	18.356	15.626			
2300	8.623	25.840	18.673	16.482			
2400	8.745	26.212	18.980	17.358			
2495	8.861	26.653	19.261	18.442			
2495	8.000	28.753	19.261	23.681			
2500	8.000	28.769	19.280	23.721			
2600	8.000	29.083	19.651	24.521			
2700	8.000	29.385	20.006	25.321			
2800	8.000	29.676	20.346	26.121			
2900	8.000	29.956	20.673	26.921			
3000	8.000	30.227	20.987	27.721			
3100	8.000	30.490	21.289	28.521			
3200	8.000	30.744	21.581	29.321			
3300	8.000	30.990	21.862	30.121			
3400	8.000	31.229	22.134	30.921			
3500	8.000	31.461	22.397	31.721			
3600	8.000	31.686	22.652	32.521			
3700	8.000	31.905	22.899	33.321			
3800	8.000	32.119	23.139	34.121			
3900	8.000	32.326	23.372	34.921			
4000	8.000	32.529	23.599	35.721			
4100	8.000	32.727	23.819	36.521			
4200	8.000	32.919	24.033	37.321			
4300	8.000	33.108	24.242	38.121			
4400	8.000	33.291	24.446	38.921			
4500	8.000	33.471	24.644	39.721			
4600	8.000	33.647	24.838	40.521			
4700	8.000	33.819	25.027	41.321			
4800	8.000	33.988	25.212	42.121			
4900	8.000	34.152	25.393	42.921			
5000	8.000	34.314	25.570	43.721			
5100	8.000	34.471	25.743	44.521			
5200	8.000	34.628	25.912	45.321			
5300	8.000	34.780	26.078	46.121			
5400	8.000	34.930	26.241	46.921			
5500	8.000	35.074	26.400	47.721			
5536.37	8.000	35.127	26.457	47.999			
5536.37	9.366	63.891	26.457	207.247			
5600	9.419	63.998	26.883	207.845			
5700	9.500	64.166	27.536	208.791			
5800	9.578	64.332	28.169	209.745			
5900	9.653	64.496	28.783	210.706			
6000	9.725	64.659	29.380	211.675			

*From change in sign of ΔF_f° of ideal gas

HAFNIUM REFERENCE STATE

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	cal/°K gfw C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	Kcal/gfw $H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0				± .010			
298.15	± .100	± .100	± .100	± .000			
1000	±1.000	± .267	± .152	± .115			
2000	±1.500	± .973	± .402	±1.140			
2033	±1.500	±1.000	± .412	±1.195			
2033	±1.500	±1.098	± .412	±1.395			
2495	±1.500	±1.307	± .550	±1.888			
2495	±1.500	±1.708	± .550	±2.888			
3000	±2.000	±1.924	± .701	±3.670			
4000	±2.000	±2.167	± .999	±4.670			
5000	±2.000	±2.613	±1.279	±6.670			
5536.37	±2.000	±2.817	±1.418	±7.743			

TABLE XXII

HAFNIUM — IDEAL MONATOMIC GAS — Hf

Reference State for Calculating ΔH_f°, ΔF_f°, and $\mathrm{Log}\ K_p$: Solid from 298.15° to 2495°K, Liquid from 2495° to 5536°K, Gas from 5536° to 6000°K.

gfw = 178.50 $T_t(l)$ = 2033° ± 200°K m.p. = 2495° ± 30°K b.p. = 5536° ± 600°K

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	$\mathrm{Log}\ K_p$
0	0.000	0.000	Infinite	-1.481	167.947	167.947	Infinite
298.15	4.972	44.645	44.645	0.000	168.000	157.869	-115.716
300	4.973	44.675	44.645	0.009	167.997	157.806	-114.956
400	5.010	46.110	44.840	0.508	167.869	154.427	-84.371
500	5.114	47.237	45.211	1.013	167.733	151.083	-66.035
600	5.285	48.184	45.629	1.533	167.601	147.766	-53.821
700	5.500	49.015	46.055	2.072	167.476	144.471	-45.104
800	5.734	49.764	46.472	2.634	167.362	141.193	-38.570
900	5.970	50.453	46.877	3.219	167.260	137.929	-33.492
1000	6.196	51.094	47.267	3.827	167.169	134.674	-29.432
1100	6.407	51.695	47.642	4.458	167.090	131.429	-26.111
1200	6.596	52.260	48.004	5.108	167.018	128.190	-23.346
1300	6.763	52.795	48.352	5.776	166.951	124.957	-21.006
1400	6.906	53.302	48.688	6.460	166.890	121.729	-19.002
1500	7.026	53.782	49.011	7.157	166.829	118.505	-17.265
1600	7.123	54.239	49.324	7.864	166.765	115.286	-15.747
1700	7.201	54.673	49.626	8.581	166.700	112.072	-14.407
1800	7.260	55.087	49.918	9.304	166.628	108.859	-13.217
1900	7.305	55.481	50.200	10.032	166.550	105.653	-12.152
2000	7.338	55.856	50.474	10.764	166.463	102.450	-11.195
2033	7.346	55.976	50.562	11.007	166.433	101.394	-10.899
2033	7.346	55.976	50.562	11.007	164.783	101.394	-10.899
2100	7.361	56.215	50.739	11.499	164.717	99.305	-10.334
2200	7.378	56.558	50.996	12.236	164.610	96.193	-9.555
2300	7.391	56.886	51.245	12.975	164.493	93.085	-8.845
2400	7.401	57.201	51.486	13.714	164.356	89.985	-8.194
2495	7.411	57.488	51.709	14.418	163.976	87.041	-7.624
2495	7.411	57.488	51.709	14.418	158.737	87.041	-7.624
2500	7.411	57.503	51.721	14.455	158.734	86.898	-7.596
2600	7.423	57.794	51.949	15.197	158.676	84.025	-7.063
2700	7.436	58.074	52.171	15.940	158.619	81.156	-6.569
2800	7.453	58.345	52.386	16.684	158.563	78.287	-6.110
2900	7.474	58.607	52.596	17.430	158.509	75.422	-5.684
3000	7.499	58.861	52.801	18.179	158.458	72.558	-5.286
3100	7.530	59.107	53.000	18.930	158.409	69.695	-4.913
3200	7.565	59.347	53.195	19.685	158.364	66.835	-4.564
3300	7.606	59.580	53.385	20.444	158.323	63.974	-4.237
3400	7.653	59.808	53.571	21.207	158.286	61.116	-3.928
3500	7.704	60.030	53.752	21.974	158.253	58.258	-3.638
3600	7.761	60.248	53.929	22.748	158.227	55.402	-3.363
3700	7.822	60.462	54.103	23.527	158.206	52.545	-3.104
3800	7.889	60.671	54.273	24.312	158.191	49.690	-2.858
3900	7.959	60.877	54.440	25.105	158.184	46.835	-2.624
4000	8.033	61.079	54.603	25.904	158.183	43.983	-2.403
4100	8.111	61.279	54.764	26.711	158.190	41.127	-2.192
4200	8.191	61.475	54.921	27.526	158.205	38.270	-1.991
4300	8.275	61.669	55.076	28.350	158.229	35.415	-1.800
4400	8.360	61.860	55.228	29.181	158.260	32.560	-1.617
4500	8.448	62.049	55.377	30.022	158.301	29.700	-1.442
4600	8.537	62.235	55.524	30.871	158.350	26.843	-1.275
4700	8.627	62.420	55.669	31.729	158.408	23.982	-1.115
4800	8.717	62.603	55.812	32.596	158.475	21.122	-0.962
4900	8.808	62.783	55.952	33.473	158.552	18.260	-0.814
5000	8.898	62.962	56.091	34.358	158.637	15.397	-0.673
5100	8.988	63.139	56.227	35.252	158.731	12.532	-0.537
5200	9.078	63.315	56.362	36.156	158.835	9.662	-0.406
5300	9.166	63.488	56.494	37.068	158.947	6.793	-0.280
5400	9.252	63.661	56.626	37.989	159.068	3.923	-0.159
5500	9.337	63.831	56.755	38.918	159.208	1.047	-0.042
5536.37	9.367	63.893	56.802	39.258	159.259	0.000	0.000
5536.37	9.367	63.893	56.802	39.258			
5600	9.419	64.000	56.883	39.856			
5700	9.500	64.167	57.009	40.802			
5800	9.578	64.333	57.134	41.756			
5900	9.653	64.498	57.258	42.717			
6000	9.725	64.661	57.380	43.686			

HAFNIUM IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal/°K gfw			Kcal/gfw			
298.15	±.000	±.002	±.002	±.000			—
1000	±.001	±.002	±.003	±.000			
2000	±.001	±.003	±.003	±.001			
2033	±.001	±.003	±.003	±.001			
2033	±.001	±.003	±.003	±.001			
2495	±.001	±.003	±.003	±.001			
2495	±.001	±.003	±.003	±.001			
3000	±.001	±.003	±.003	±.001			
4000	±.003	±.003	±.003	±.003			
5000	±.006	±.004	±.003	±.007			
5536.37	±.009	±.005	±.003	±.011			
5536.37	±.009	±.005	±.003	±.011			
6000	±.011	±.006	±.003	±.015			

gfw = 192.2

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite				Infinite
298.15	4.969	46.242	46.242	0.000			
300	4.969	46.273	46.242	0.009			
400	4.976	47.703	46.437	0.506			
500	5.007	48.816	46.806	1.005			
600	5.075	49.734	47.219	1.509			
700	5.180	50.524	47.636	2.021			
800	5.314	51.224	48.042	2.546			
900	5.465	51.859	48.431	3.085			
1000	5.622	52.443	48.804	3.639			
1100	5.780	52.986	49.159	4.209			
1200	5.933	53.495	49.500	4.795			
1300	6.079	53.976	49.826	5.396			
1400	6.215	54.432	50.139	6.010			
1500	6.340	54.865	50.439	6.638			
1600	6.455	55.278	50.729	7.278			
1700	6.560	55.672	51.008	7.929			
1800	6.654	56.050	51.278	8.590			
1900	6.739	56.412	51.539	9.259			
2000	6.815	56.760	51.791	9.937			
2100	6.883	57.094	52.036	10.622			
2200	6.944	57.415	52.273	11.314			
2300	6.999	57.725	52.503	12.011			
2400	7.048	58.024	52.727	12.713			
2500	7.093	58.313	52.945	13.420			
2600	7.133	58.592	53.157	14.132			
2700	7.170	58.862	53.363	14.847			
2800	7.204	59.123	53.564	15.566			
2900	7.235	59.377	53.760	16.288			
3000	7.263	59.622	53.952	17.012			
3100	7.289	59.861	54.138	17.740			
3200	7.313	60.093	54.321	18.470			
3300	7.336	60.318	54.499	19.203			
3400	7.357	60.537	54.674	19.937			
3500	7.377	60.751	54.844	20.674			
3600	7.396	60.959	55.011	21.413			
3700	7.413	61.162	55.175	22.153			
3800	7.430	61.360	55.335	22.895			
3900	7.446	61.553	55.492	23.639			
4000	7.461	61.742	55.646	24.385			
4100	7.475	61.926	55.797	25.131			
4200	7.489	62.107	55.945	25.880			
4300	7.503	62.283	56.090	26.629			
4400	7.516	62.456	56.233	27.380			
4500	7.529	62.625	56.373	28.132			
4600	7.541	62.790	56.511	28.886			
4700	7.554	62.953	56.646	29.641			
4800	7.567	63.112	56.779	30.397			
4900	7.579	63.268	56.910	31.154			
5000	7.592	63.421	57.039	31.913			
5100	7.605	63.572	57.165	32.672			
5200	7.618	63.719	57.290	33.434			
5300	7.632	63.865	57.413	34.196			
5400	7.646	64.007	57.533	34.960			
5500	7.661	64.148	57.652	35.725			
5600	7.676	64.286	57.770	36.492			
5700	7.692	64.422	57.885	37.261			
5800	7.708	64.556	57.999	38.031			
5900	7.726	64.688	58.111	38.802			
6000	7.744	64.818	58.222	39.576			

IRIDIUM IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	cal/°K gfw C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	Kcal/gfw $H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	±.000	±.002	±.002	±.000			
1000	±.000	±.002	±.003	±.000			
2000	±.001	±.003	±.003	±.001			
3000	±.001	±.003	±.003	±.001			
4000	±.001	±.003	±.003	±.002			
5000	±.002	±.003	±.003	±.003			
6000	±.004	±.004	±.003	±.006			

7. Iridium

The ideal gas thermodynamic functions in Table XXIII were calculated with the energy levels given by Moore[221] and the computer program discussed in section III-D. Uncertainty estimates are summarized on the back of the table.

8. Magnesium

a. Crystal Structure and Melting Point

Elemental magnesium has a hexagonal, close-packed structure from room temperature to its melting point.[57] The latter temperature was taken to be 923° ± 3°K, in agreement with other recent compilations.[76, 156, 77, 56, 78]

b. Thermodynamic Properties

1) Heat of fusion

Kelley[137] reviewed the early data on the heat of fusion of magnesium which was derived from phase studies of binary alloys. He gave a mean value of 2.16 Kcal/gfw. Stull and McDonald[224] made heat content measurements on solid and liquid magnesium, and reported the heat of fusion to be 2.14 ± 0.05 Kcal/gfw. The Bureau of Standards[78] reviewed available solid and liquid heat content measurements for the period up to 1959 and arrived at a value of 2.127 Kcal/gfw. The value of 2.127 ± 0.03 Kcal/gfw was adopted for the heat of fusion of magnesium in the present work.

Other determinations of the heat of fusion of magnesium included the following:

Source	Heat of Fusion (Kcal/gfw)
Wittig (reported by Kubaschewski[79])	1.83 ± 0.09
Reinartz (reported by Kubaschewski[79])	2.03 ± 0.08
Treadwell[225]	1.37
Treadwell[226]	1.04
Zalesinski and Zulinski[138]	1.12
Awbery and Griffiths[227]	1.13
Roos[228]	1.70

[224] Stull, D.R. and R. McDonald, J. Am. Chem. Soc. 77, 5293 (1955).

[225] Treadwell, W.D., Schw. Arac. angew. Wiss. Technik 6, 69 (1940).

[226] Treadwell, W.D., A. Amann, and T. Zurrer, Helv. Chim. Acta 19, 1255 (1936).

[227] Awbery, J.H. and E. Griffiths, Proc. Phys. Soc. (London) 38, 378 (1926).

[228] Roos, G.D., Z. anorg. Chem. 94, 329 (1916).

Kubaschewski[79] arrived at a value for the heat of fusion of 2.00 ± 0.12 Kcal/gfw from these other results plus the analysis of Kelley.[56]

2) Entropy and heat content at 298.15 °K

The reported entropy and heat content of magnesium at 298.15 °K have been based on the measurements of Craig et al[229] (12 ° to 320 °K); Smith[230] (1 ° to 20 °K); Logan, Clement, and Jeffers[231] (3 ° to 13 °K); and Estermann, Friedberg, and Goldman[206] (1.8 ° to 4.2 °K). On the basis of these data, the Bureau of Standards[78] selected S°_{298} to be 7.800 ± 0.05 e.u., while Dergazarian et al[75] (JANAF Interim Thermochemical Panel Tables) selected the value 7.824 e.u. The difference is due to variations in adopted numerical techniques for smoothing and joining the low-temperature data to high-temperature data. Craig et al[229] calculated S°_{298} to be 7.81 e.u. by graphical integration (using an unexplained correction factor of 1.0041).[76] A value of 7.800 ± 0.03 was adopted for the present work and was used to calculate $H^\circ_{298} - H^\circ_0$ equal to 1195 cal/gfw.

Other low-temperature data for the heat capacity of magnesium have been given by Mannchen and Bornkessel[232] (12 ° to 300 °K), Clusius and Vaughen[140] (11 ° to 228 °K), Eastman and Rodebush[144] (75 ° to 289 °K), and Nernst and Schwers[233] (27 ° to 94 °K).

3) High-temperature heat content

Heat contents for magnesium from 298.15 °K to the melting point have been based on the measurements of Saba, Sterrett, Craig, and Wallace[234] (298 ° to 543 °K), and Stull and McDonald[224] (700 ° to 1100 °K). These data have been smoothed and joined by the Bureau of Standards.[78] The Bureau's compilation for magnesium up to the melting point was accepted with a re-calculation to fit the format used herein. In the NBS compilation, the low-temperature data (in cal/gfw) were joined smoothly at 475 °K with the high-temperature heat content equation

$$H^\circ_T - H^\circ_{298} = 4.689T + 1.718 \times 10^{-3}T^2 - 2.0776 \times 10^4 T^{-1} - 1481. \quad (142)$$

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229 Craig, K.S., C.A. Krier, L.W. Coffer, E.A. Bates, and W.E. Wallace, J. Am. Chem. Soc. 76, 238 (1954).

230 Smith, P.L., Phil. Mag. 46, 744 (1955).

231 Logan, J.K., J.R. Clement, and H.R. Jeffers, Phys. Rev. 105, 1435 (1957).

232 Mannchen, W. and K. Bornkessel, Z. Naturforsch, 14a, 925 (1959).

233 Nernst, W. and F. Schwers, Sitzb. Konig preuss. Akad. Wiss. 1, 355 (1914).

234 Saba, W.G., K.F. Sterrett, R.S. Craig, and W.E. Wallace, J. Am. Chem. Soc. 79, 3637 (1957).

The accuracy of the tabulated heat contents was taken to be ± 1 percent. Other recent compilations using different smoothing procedures have used the same original data sources to derive slightly different thermodynamic functions.

Stull and McDonald[224] measured the heat content of liquid magnesium up to 1100 °K and represented their data for the liquid phase (in cal/° K g) by the equation.

$$H_T^o - H_{298}^o = 0.2176T + 5.35 \times 10^{-5}T^2 + 484.63\ T^{-1} + 16.851. \qquad (143)$$

However, within the error of the measurements (± 2 percent) their data could be equally well-represented by a constant heat capacity of 7.8 cal/° K gfw, so that the heat content in cal/° K gfw from 923 ° to 1377 °K could be represented by

$$H_T^o - H_{298}^o = 7.8\ T - 781\ . \qquad (144)$$

Above 1100 °K, the uncertainty in the heat content was assumed to increase at the rate of 0.015 Kcal/gfw per 100 °C of temperature increase.

High-temperature heat content or heat capacity measurements have also been made on magnesium by Poppema and Jaeger[235] (373 ° to 823 °K), Honda and Tokunaga[236] (298 °K), Seekamp[237] (271 ° to 773 °K), Awbery and Griffiths[227] (525 ° to 1023 °K), Eastman, Williams, and Young[136] (373 ° to 888 °K), Schubel[238] (373 ° to 773 °K), Magnus[239] (373 ° to 812 °K), Kubaschewski[240] (923 ° to 1123 °K), Lorenz[241] (293 ° to 403 °K), Losano[242] (293 ° to 573 °K), Stücker[243] (293 ° to 923 °K), and Zalesinski and Zulinski[138] (295 ° to 1048 °K).

4) Heat of formation of the monatomic gas

The tabulated free-energy functions were used with vapor pressure data from the following sources to calculate the indicated heats of formation at 298.15 °K by use of the Third Law Method:

[235] Poppema, T.J. and F.M. Jaeger, Proc. Acad. Sci. (Amsterdam) 38, 510 (1935).

[236] Honda, K. and M. Tokunaga, Sci. Repts. Tohoku Imp. Univ. 23, 816 (1935).

[237] Seekamp, H., Z. anorg. u. allgem. Chem. 195, 345 (1931).

[238] Schubel, P., Z. anorg. Chem. 87, 81 (1914).

[239] Magnus, A., Habilitationsschrift, Eberhard-Karls Universitat, Tübingen (1910).

[240] Kubaschewski, O., Z. Metallkunde 41, 445 (1950).

[241] Lorenz, L., Poggendorf's Ann. 13, 422 (1881).

[242] Losano, L., Ind. Chim. 5, 145 (1930).

[243] Stücker, N., Sitzb. konig. Akad. Wiss. 114, 657 (1905).

Source of Vapor Pressure Data	Temperature Range (°K)	Calculated ΔH°_{f298} (Kcal/gfw)
Smith and Smythe[152]	626-818	35.130 ± 0.020
Vetter and Kubaschewski[244]	973-1073	35.180 ± 0.110
Schneider and Stoll[245]	917-1002	35.260 ± 0.100
Schneider and Esch[246]	1376 (b.p.)	35.320
Coleman and Egerton[247]	700-738	35.300 ± 0.040
Baur and Brunner[92]	926-1283	35.355 ± 0.400
Leitgebel[248]	1370 (b.p.)	35.190
Hartmann and Schneider[148]	1009-1293	35.660 ± 0.250
Ruff and Hartmann[153]	911-1344	34.910 ± 1.500
Greenwood[249]	1393 (b.p.)	35.480
Ditte[250]	1383 (b.p.)	35.700
Scheil and Wolf[251]	1016-1102	35.510 ± 0.040
Wejnarth[252]	unavailable	---

With the exception of the results of Smith and Smythe[152] and of Scheil and Wolf,[251] all of these calculations were based on the original data points. For the former only was an equation available; and for the latter, the data were taken from graphs.

[244]Vetter, F.A. and O. Kubaschewski, Z. Elektrochem. 57, 243 (1953).

[245]Schneider, A. and E.K. Stoll, Z. Elektrochem. 47, 519 (1941).

[246]Schneider, A. and V. Esch, Z. Elektrochem. 45, 888 (1939).

[247]Coleman, F.F. and A.C. Egerton, Phil. Trans. Roy. Soc. London 234A, 177 (1935).

[248]Leitgebel, W., Z. anorg. Chem. 202, 305 (1931).

[249]Greenwood, H., Proc. Roy. Soc. (London) 83A, 413 (1910).

[250]Ditte, B., Compt. Rend 73, 111 (1871).

[251]Scheil, E. and F. Wolf, Z. Metallkunde 50, 229 (1959).

[252]Wejnarth, A., Tek. Tid. 72, 33 (1942).

The value of ΔH°_{f298} adopted was an average of the above values, excluding the results of Ruff and Hartmann[153] and of Ditte.[250] This average value is 35.340 ± 0.250 Kcal/gfw. The error given was based on the spread in reported vapor pressures, and did not include uncertainties in condensed phase free-energy functions. The normal boiling point of magnesium was calculated to be 1377° ± 6°K. The uncertainty in the boiling-point value was estimated from an uncertainty of 0.21 e.u. in ΔS°_v and an uncertainty of 0.40 Kcal/gfw in ΔH°_v at the normal boiling point where ΔH_v equals 30.740 Kcal/gfw.

5) Thermodynamic functions

The reference state thermodynamic functions of magnesium are given in Table XXIV. The ideal monatomic gas thermodynamic functions of magnesium given in Table XXV were calculated using all the energy levels listed by Moore.[52] Uncertainty estimates are summarized on the back of the tables. $H^\circ_{298} - H^\circ_0$ was found to be 1,481 cal/mole for the ideal gas.

TABLE XXIV

MAGNESIUM | REFERENCE STATE | Mg

Reference State for Calculating ΔH_f°, ΔF_f°, and $\text{Log } K_p$: Solid from 298.15° to 923°K, Liquid from 923° to 1377°K, Gas from 1377° to 6000°K.

gfw = 24.32 | m.p. = 923° ± 3°K | b.p. = 1377° + 6°K

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-1.195			
298.15	5.951	7.800	7.800	0.000			
300	5.957	7.836	7.800	0.011			
400	6.212	9.587	8.037	0.620			
500	6.490	11.001	8.492	1.254			
600	6.808	12.212	9.013	1.919			
700	7.137	13.286	9.548	2.616			
800	7.470	14.261	10.077	3.347			
900	7.807	15.160	10.593	4.110			
923	7.885	15.358	10.709	4.291			
923	7.800	17.662	10.709	6.418			
1000	7.800	18.287	11.268	7.019			
1100	7.800	19.030	11.940	7.799			
1200	7.800	19.709	12.560	8.579			
1300	7.800	20.333	13.134	9.359			
1377	7.800	20.778	13.545	9.960			
1377	4.968	43.102	13.545	40.700			
1400	4.968	43.188	14.035	40.814			
1500	4.968	43.531	15.990	41.311			
1600	4.968	43.851	17.721	41.808			
1700	4.968	44.153	19.268	42.305			
1800	4.968	44.437	20.659	42.801			
1900	4.968	44.705	21.917	43.298			
2000	4.969	44.960	23.062	43.795			
2100	4.969	45.202	24.111	44.292			
2200	4.970	45.434	25.075	44.789			
2300	4.972	45.655	25.965	45.286			
2400	4.974	45.866	26.790	45.783			
2500	4.978	46.069	27.557	46.281			
2600	4.983	46.265	28.273	46.779			
2700	4.989	46.453	28.943	47.278			
2800	4.998	46.634	29.571	47.777			
2900	5.009	46.810	30.163	48.277			
3000	5.023	46.980	30.720	48.779			
3100	5.040	47.145	31.248	49.282			
3200	5.060	47.305	31.747	49.787			
3300	5.085	47.461	32.220	50.294			
3400	5.114	47.614	32.672	50.804			
3500	5.148	47.762	33.100	51.317			
3600	5.186	47.908	33.510	51.834			
3700	5.229	48.051	33.901	52.354			
3800	5.278	48.191	34.275	52.880			
3900	5.332	48.328	34.634	53.410			
4000	5.392	48.464	34.978	53.946			
4100	5.457	48.598	35.308	54.489			
4200	5.528	48.730	35.626	55.038			
4300	5.604	48.861	35.933	55.594			
4400	5.686	48.991	36.228	56.159			
4500	5.773	49.120	36.513	56.732			
4600	5.866	49.248	36.788	57.314			
4700	5.964	49.375	37.055	57.905			
4800	6.067	49.502	37.313	58.507			
4900	6.176	49.628	37.563	59.119			
5000	6.289	49.754	37.806	59.742			
5100	6.407	49.879	38.040	60.377			
5200	6.530	50.005	38.270	61.024			
5300	6.658	50.131	38.493	61.683			
5400	6.790	50.256	38.709	62.355			
5500	6.927	50.382	38.920	63.041			
5600	7.069	50.508	39.126	63.741			
5700	7.215	50.635	39.327	64.455			
5800	7.366	50.761	39.522	65.184			
5900	7.522	50.889	39.715	65.929			
6000	7.682	51.016	39.901	66.669			

MAGNESIUM REFERENCE STATE

SUMMARY OF UNCERTAINTY ESTIMATES

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	±.030	±.030	±.030	±.000			
923	±.060	±.060	±.020	±.040			
923	±.160	±.090	±.020	±.070			
1377	±.600	±.210	±.070	±.200			
1377	±.000	±.002					
2000	±.000	±.002					
3000	±.001	±.002					
4000	±.002	±.003					
5000	±.002	±.003					
6000	±.002	±.003					

<u>TABLE XXV</u>

MAGNESIUM — IDEAL MONATOMIC GAS — Mg

Reference State for Calculating ΔH_f°, ΔF_f°, and $\text{Log } K_p$: Solid from 298.15° to 923° K, Liquid from 923° to 1377° K, Gas from 1377° to 6000° K.

gfw = 24.32 — m.p. = 923° ± 3° K — b.p. = 1377° ± 6° K

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-1.481	35.054	35.054	Infinite
298.15	4.968	35.504	35.504	0.000	35.340	27.080	-19.849
300	4.968	35.535	35.504	0.009	35.338	27.029	-19.690
400	4.968	36.964	35.699	0.506	35.226	24.275	-13.263
500	4.968	38.073	36.067	1.003	35.089	21.553	-9.420
600	4.968	38.978	36.479	1.500	34.921	18.860	-6.869
700	4.968	39.744	36.892	1.996	34.720	16.199	-5.057
800	4.968	40.408	37.291	2.493	34.486	13.569	-3.707
900	4.968	40.993	37.671	2.990	34.220	10.970	-2.664
923	4.968	41.118	37.755	3.104	34.153	10.377	-2.457
923	4.968	41.118	37.755	3.104	32.026	10.377	-2.457
1000	4.968	41.516	38.029	3.487	31.808	8.580	-1.875
1100	4.968	41.990	38.368	3.984	31.525	6.269	-1.245
1200	4.968	42.422	38.688	4.481	31.242	3.986	-0.726
1300	4.968	42.820	38.991	4.977	30.959	1.726	-0.290
1377	4.968	43.102	39.210	5.360	30.740	0.000	0.000
1377	4.968	43.102	39.210	5.360			
1400	4.968	43.188	39.278	5.474			
1500	4.968	43.531	39.550	5.971			
1600	4.968	43.851	39.809	6.468			
1700	4.968	44.153	40.056	6.965			
1800	4.968	44.437	40.291	7.461			
1900	4.968	44.705	40.517	7.958			
2000	4.969	44.960	40.732	8.455			
2100	4.969	45.202	40.940	8.952			
2200	4.970	45.434	41.139	9.449			
2300	4.972	45.655	41.330	9.946			
2400	4.974	45.866	41.515	10.443			
2500	4.978	46.069	41.693	10.941			
2600	4.983	46.265	41.865	11.439			
2700	4.989	46.453	42.032	11.938			
2800	4.998	46.634	42.193	12.437			
2900	5.009	46.810	42.349	12.937			
3000	5.023	46.980	42.500	13.439			
3100	5.040	47.145	42.648	13.942			
3200	5.060	47.305	42.791	14.447			
3300	5.085	47.461	42.930	14.954			
3400	5.114	47.614	43.965	15.464			
3500	5.148	47.762	43.197	15.977			
3600	5.186	47.908	43.326	16.494			
3700	5.229	48.051	43.452	17.014			
3800	5.278	48.191	43.575	17.540			
3900	5.332	48.328	43.695	18.070			
4000	5.392	48.464	43.813	18.606			
4100	5.457	48.598	43.928	19.149			
4200	5.528	48.730	44.040	19.698			
4300	5.604	48.861	44.151	20.254			
4400	5.686	48.991	44.260	20.819			
4500	5.773	49.120	44.366	21.392			
4600	5.866	49.248	44.471	21.974			
4700	5.964	49.375	44.574	22.565			
4800	6.067	49.502	44.675	23.167			
4900	6.176	49.628	44.775	23.779			
5000	6.289	49.754	44.873	24.402			
5100	6.407	49.879	44.970	25.037			
5200	6.530	50.005	45.066	25.684			
5300	6.658	50.131	45.160	26.343			
5400	6.790	50.256	45.253	27.015			
5500	6.927	50.382	45.346	27.701			
5600	7.069	50.508	45.437	28.401			
5700	7.215	50.635	45.527	29.115			
5800	7.366	50.761	45.616	29.844			
5900	7.522	50.889	45.704	30.589			
6000	7.682	51.016	45.792	31.349			

MAGNESIUM IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	cal/°K gfw C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	Kcal/gfw $H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	±.000	±.002	±.000	±.000	±.250	±.260	±.190
923					±.290	±.270	±.060
923					±.320	±.270	±.060
1000	±.000	±.002	±.002	±.000			
1377					±.450	±.350	±.060
2000	±.000	±.002	±.003	±.001			
3000	±.001	±.002	±.003	±.001			
4000	±.002	±.003	±.003	±.002			
5000	±.002	±.003	±.003	±.004			
6000	±.002	±.003	±.003	±.005			

MANGANESE

TABLE XXVI

IDEAL MONATOMIC GAS

gfw = 54.94

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite				Infinite
298.15	4.968	41.494	41.494	0.000			
300	4.968	41.525	41.494	0.009			
400	4.968	42.954	41.689	0.506			
500	4.968	44.063	42.057	1.003			
600	4.968	44.968	42.469	1.500			
700	4.968	45.734	42.882	1.996			
800	4.968	46.398	43.281	2.493			
900	4.968	46.983	43.660	2.990			
1000	4.968	47.506	44.019	3.487			
1100	4.968	47.980	44.358	3.984			
1200	4.968	48.412	44.678	4.481			
1300	4.968	48.810	44.981	4.977			
1400	4.968	49.178	45.268	5.474			
1500	4.968	49.521	45.540	5.971			
1600	4.969	49.841	45.799	6.468			
1700	4.969	50.143	46.046	6.965			
1800	4.971	50.427	46.281	7.462			
1900	4.973	50.695	46.507	7.959			
2000	4.977	50.951	46.722	8.456			
2100	4.982	51.194	46.930	8.954			
2200	4.991	51.426	47.129	9.453			
2300	5.002	51.648	47.320	9.953			
2400	5.018	51.861	47.505	10.454			
2500	5.040	52.066	47.684	10.956			
2600	5.067	52.264	47.856	11.462			
2700	5.101	52.456	48.023	11.970			
2800	5.142	52.642	48.184	12.482			
2900	5.193	52.824	48.341	12.999			
3000	5.253	53.001	48.494	13.521			
3100	5.322	53.174	48.642	14.050			
3200	5.403	53.344	48.766	14.586			
3300	5.495	53.512	48.927	15.131			
3400	5.598	53.677	49.064	15.685			
3500	5.713	53.841	49.198	16.251			
3600	5.841	54.004	49.330	16.828			
3700	5.981	54.166	49.458	17.419			
3800	6.133	54.327	49.584	18.028			
3900	6.297	54.489	49.708	18.646			
4000	6.473	54.650	49.829	19.285			
4100	6.661	54.813	49.949	19.941			
4200	6.859	54.975	50.067	20.617			
4300	7.068	55.139	50.183	21.313			
4400	7.287	55.304	50.297	22.031			
4500	7.515	55.471	50.410	22.771			
4600	7.751	55.638	50.522	23.534			
4700	7.995	55.808	50.633	24.322			
4800	8.244	55.979	50.742	25.134			
4900	8.500	56.151	50.851	25.971			
5000	8.759	56.325	50.959	26.834			
5100	9.022	56.502	51.066	27.723			
5200	9.288	56.679	51.172	28.638			
5300	9.554	56.859	51.278	29.580			
5400	9.821	57.040	51.383	30.549			
5500	10.088	57.222	51.487	31.545			
5600	10.352	57.407	51.591	32.567			
5700	10.614	57.592	51.695	33.615			
5800	10.873	57.779	51.798	34.689			
5900	11.127	57.967	51.901	35.789			
6000	11.376	58.156	52.004	36.914			

MANGANESE IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	cal/°K gfw			Kcal/gfw			Log K_p
	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	
298.15	±.000	±.002	±.002	±.000			
1000	±.000	±.002	±.002	±.000			
2000	±.000	±.002	±.003	±.000			
3000	±.000	±.002	±.003	±.001			
4000	±.001	±.003	±.003	±.001			
5000	±.002	±.003	±.003	±.002			
6000	±.003	±.003	±.003	±.004			

9. Manganese

The ideal gas thermodynamic functions in Table XXVI were calculated with the energy levels given by Moore[253] and the computer program discussed in section III-D. Uncertainty estimates are summarized on the back of the table.

[253]Moore, C.E., Nat. Bur. Stds. Circ. 467, vol 2 (15 August 1952).

10. Molybdenum

The stable form of solid molybdenum at 25 °C is the body-centered cubic crystal.[254-256] There appears to be no conclusive evidence for solid-state transitions although the existence of a face-centered cubic modification has been reported.[257] The body-centered cubic form has been taken as the stable form from room temperature to the melting point in the present work. The melting point of molybdenum is 2617° ±10 °C, and the estimated standard boiling point is 4692° ±300 °C.

a. The Melting Point of Molybdenum

The absolute value of the melting point of molybdenum has been somewhat in doubt, but the "best" value has been taken to be 2617° ±10 °C by several workers.[76,77,56] The most exhaustive study of the melting point appeared to be that of Worthing[258,259] who reported a value of 2622° ±10 °C. Worthing[259] discussed the results of earlier workers whose values ranged from 2562° to 2597 °C. Melting-point values were also discussed in two recent general works dealing with molybdenum.[254,256]

The heat of fusion has not been directly established. Estimated values found in the literature included the following:

6660 cal/g atom	(Ref. 191)
6650 cal/g atom	(Ref. 56)
6600 cal/g atom	(Ref. 77)
3000 cal/g atom	(Ref. 256)
4800 cal/g atom	(Ref. 254)
6650 cal/g atom	(Ref. 76)
6700 cal/g atom	(Ref. 260)
8380 cal/g atom	(Ref. 261)

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254 Northcott, L., Molybdenum, Butterworths, London (1956).

255 Lu, S.S. and Y.L. Chang, Proc. Phys. Soc. (London) 53, 517 (1941).

256 Agte, C. and J. Vacek, Wolfram and Molybdan, Akademic Verlag, Berlin (1959).

257 Aggarwal, P.S. and A. Goswami, Proc. Phys. Soc. (London) 70B, 708 (1957).

258 Worthing, A.G., J. Franklin Inst. 199, 549 (1925).

259 Worthing, A.G., Phys. Rev. 25, 846 (1925).

260 Molybdenum Metal, Climax Molybdenum Co., New York (1960).

261 Jones, H.A., I. Langmuir, and G.M. J. MacKay, Phys. Rev. 30, 201 (1927).

In the absence of conclusive experimental data, an estimated ΔH of fusion of 6650 cal/g atom was chosen for the present compilation. This value was based on an assumed entropy of fusion of 2.3 e.u. An uncertainty of ±1000 cal/g atom was arbitrarily assigned to the ΔH of fusion at the melting point.

b. The Standard Heat of Formation at 298.15°K (ΔH°_{f298})

Vapor pressure measurements for solid molybdenum have been reported by Jones, Langmuir, and MacKay,[261] by Norris and Worthing,[262] and by Edwards, Johnston, and Blackburn.[263] A ΔH°_{f298} value of 158,200 ± 800 cal/g atom was calculated using the vapor pressure values of Edwards and co-workers,[263] and the free-energy functions from the present compilation. Norris and Worthing[262] did not report actual experimental vapor pressure values, and the data of Jones and co-workers[261] led to a rather marked temperature dependence of ΔH°_{f298}. The latter two studies were therefore given no weight in evaluating ΔH°_{f298}.

c. The Boiling Point of Molybdenum

The boiling point of molybdenum had not been clearly established. Estimated and/or quoted values ranged from 3650° to 5697°C; e.g.:

3560°C	(Ref. 264)
3700°C	(Ref. 256)
4651°C	(Ref. 76)
4804°C	(Ref. 191)
4827°C	(Ref. 77)
5560°C	(Ref. 260)
5687°C	(Ref. 261)

From a calculated ΔH°_{f298} value of 158,200 ±800 cal/g atom and free-energy functions for the gas and condensed phases from the present compilation, a standard boiling point of 4692° ±300°C was calculated in the present work.

[262] Norris, L. and A.G. Worthing, Phys. Rev. 44, 323 (1933).

[263] Edwards, J.W., H.L. Johnston, and P.E. Blackburn, J. Am. Chem. Soc., 74, 1539 (1952).

[264] Sidgwick, N.V., Chemical Elements and Their Compounds, vol. 2, Oxford University Press, London (1950).

The heat of vaporization at the standard boiling point was then estimated from the above value of ΔH°_{f298} and the enthalpy functions for the gaseous and condensed phases at the standard boiling temperature. The value thus calculated was 141,300 ± 10,000 cal/g atom.

In Table XXVII are summarized the heats of transformation for the various phase changes of molybdenum.

TABLE XXVII

TRANSFORMATION DATA FOR MOLYBDENUM

Transition	Temperature (°K)	ΔH (cal/g atom)
solid → liquid	2890 ± 10	6650 ± 1000
liquid → gas	4965 ± 300	141,300 ± 10,000
solid → gas	298.15	158,200 ± 800

d. Calculation of Thermodynamic Functions for Condensed Phases of Molybdenum

Recent compilations of the thermodynamic functions of solid and liquid molybdenum included those of Stull and Sinke,[77] Hultgren,[76] and Kelley.[56] Those three compilations were in essential agreement but did not take into account the recent heat capacity measurements of Rasor and McClelland[27, 157] in the temperature range from about 1500°K to the melting point. The values of enthalpy and entropy at 298.15°K were as follows:

$H^{\circ}_{298} - H^{\circ}_{0} = 1092$ cal/g atom (Refs. 76, 77)

$S^{\circ}_{298} = 6.83$ e.u. (Refs. 76, 77, 265).

For purposes of discussion, the thermodynamic properties of solid molybdenum will be considered first over the temperature range from 298.15° to about 1500°K, and then from about 1500°K to the melting point.

[265] Clusius, K. and P. Franzosini, Z. Naturforsch. A14, 99 (1959).

The enthalpy functions for solid molybdenum (i.e., $H^\circ_T - H^\circ_{298}$), for the temperature range from 298.15° to 1500°K in the present table, were those of Stull and Sinke;[77] they are almost identical to those of Hultgren[76] and Kelley.[56] The tabular entropy values, S°_T , were calculated by the method of Kelley.[56] Values for $-\left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)$ were then calculated from equation (108).

The tabular values of C°_p over this temperature range were those of Stull and Sinke[77] and Hultgren.[76]

For the temperature range from 1500°K to the melting point, other compilers[56,76,77] chose a linear function of C°_p based on enthalpy measurements of Kothen[266] and Redfield and Hill[267] over portions of this temperature range. However, Rasor and McClelland[27,157] have measured C°_p values over the whole temperature range and reported an appreciable deviation from linearity. The heat capacity values of Rasor and McClelland gave a poor "fit" with a $C^\circ_p(T)$ function of the form

$$A + BT + CT^{-2} \quad ,$$

but gave a very good "fit" with a function of the form

$$A + BT + CT^2 \quad .$$

The equation employed herein was

$$C^\circ_p = 6.026 - 0.217 \times 10^{-3}\,T + 0.0880 \times 10^{-5}\,T^2 \quad . \tag{145}$$

This equation gave C°_p values which join those of the low range (298.15° to 1500°K) smoothly at 1500°K.

Tabular values of C°_p were calculated with equation (145). The equation was then used to calculate tabular values of entropy and enthalpy over the temperature range from 1600°K to the melting point. The entropy and enthalpy equations were

$$S^\circ_T = 6.026 \ln T - 0.217 \times 10^{-3}\,T + 0.440 \times 10^{-5}\,T^2 - 27.5066 \,, \tag{146}$$

[266] Kothen, C., The High Temperature Heat Contents of Molybdenum and Titanium and the Low Temperature Heat Capacities of Titanium, Ph.D. Thesis, Ohio State Univ. (1952); Dissertation Abstracts 17, 2842 (1957); Univ. Mich., Microfilm, Ann Arbor, Pub. No. 23697.

[267] Redfield, T.A. and J.H. Hill, U.S. Atomic Energy Commission, Rept. ORNL – 1087, Oak Ridge National Lab. (24 September 1951).

and

$$H^\circ_T - H^\circ_{298} = 6.026\,T - 10.85 \times 10^{-5}\,T^2 + 29.333 \times 10^{-8}T^3 - 1785. \qquad (147)$$

The values of the last constants in the above equations were evaluated from the tabular values of S°_T and $H^\circ_T - H^\circ_{298}$ at 1500 °K. The free-energy function for solid molybdenum in this temperature range was then calculated using equation (108).

The heat capacity of liquid molybdenum was taken to be a constant value of 10.00 cal/°K g atom. This value was an estimate[76] since an experimental determination did not appear to have ever been made. Entropy and enthalpy values for liquid molybdenum were calculated using this value of C°_p according to equations (138) and (139).

The values of the constants C_1 and C_2 in equations (138) and (139) were evaluated from the tabular values of S°_T and $H^\circ_T - H^\circ_{298}$ for liquid molybdenum at the melting point. The free-energy function for liquid molybdenum was evaluated in the same manner as that used for the corresponding function of solid molybdenum.

e. Calculation of Thermodynamic Functions for Gaseous Molybdenum

Thermodynamic properties for the ideal monatomic gas were calculated using the spectroscopic energy levels listed by Moore.[52] Energy levels and J values not definitely established in these tables were estimated. The equations employed in these calculations have been discussed in two recent publications[75, 51] and are summarized in section III-D.

The ΔH°_f, ΔF°_f, and $\log_{10}K_p$ functions of gaseous molybdenum were calculated by the methods in section III-D.

f. Uncertainty in Condensed Phase Functions

The basic data for molybdenum included both heat capacity and enthalpy measurements.[173, 194, 243, 27] Heat capacities could be calculated from measured enthalpies; therefore, for the present compilation, uncertainties were assigned to C°_p values and these uncertainties then used in calculating uncertainties in the other thermodynamic functions. These uncertainty estimates are summarized on the back of Table XXVIII.

TABLE XXVIII

MOLYBDENUM — REFERENCE STATE — Mo

Reference State for Calculating ΔH_f°, ΔF_f°, and Log K_p : Solid from 298.15° to 2890°K, Liquid from 2890° to 4965°K, Gas from 4965° to 6000°K.

gfw = 95.95 — m.p. = 2890° ± 10°K — b.p. = 4965° ± 300°K

T, °K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal/gfw)	ΔH_f° (Kcal/gfw)	ΔF_f° (Kcal/gfw)	Log K_p
0	0.000	0.000	Infinite	-1.092			
298.15	5.680	6.830	6.830	0.000			
300	5.690	6.865	6.830	0.011			
400	5.970	8.545	7.057	0.595			
500	6.150	9.905	7.499	1.203			
600	6.280	11.035	7.993	1.825			
700	6.350	12.013	8.499	2.460			
800	6.440	12.868	8.993	3.100			
900	6.550	13.633	9.467	3.750			
1000	6.700	14.329	9.919	4.410			
1100	6.860	14.977	10.349	5.090			
1200	7.050	15.586	10.761	5.790			
1300	7.240	16.162	11.154	6.510			
1400	7.450	16.710	11.531	7.250			
1500	7.680	17.227	11.894	8.000			
1600	7.932	17.731	12.244	8.780			
1700	8.200	18.220	12.580	9.587			
1800	8.486	18.697	12.907	10.421			
1900	8.791	19.163	13.224	11.285			
2000	9.112	19.622	13.532	12.180			
2100	9.451	20.075	13.833	13.108			
2200	9.808	20.523	14.127	14.071			
2300	10.182	20.967	14.415	15.070			
2400	10.574	21.409	14.697	16.107			
2500	10.983	21.849	14.975	17.185			
2600	11.411	22.288	15.247	18.305			
2700	11.855	22.727	15.516	19.468			
2800	12.317	23.166	15.782	20.676			
2890	12.749	23.563	16.018	21.804			
2890	10.000	25.864	16.018	28.454			
2900	10.000	25.899	16.053	28.554			
3000	10.000	26.238	16.387	29.554			
3100	10.000	26.566	16.710	30.554			
3200	10.000	26.883	17.022	31.554			
3300	10.000	27.191	17.326	32.554			
3400	10.000	27.489	17.620	33.554			
3500	10.000	27.779	17.906	34.554			
3600	10.000	28.061	18.185	35.554			
3700	10.000	28.335	18.456	36.554			
3800	10.000	28.602	18.719	37.554			
3900	10.000	28.861	18.975	38.554			
4000	10.000	29.115	19.226	39.554			
4100	10.000	29.361	19.470	40.554			
4200	10.000	29.602	19.708	41.554			
4300	10.000	29.838	19.942	42.554			
4400	10.000	30.068	20.169	43.554			
4500	10.000	30.292	20.391	44.554			
4600	10.000	30.512	20.609	45.554			
4700	10.000	30.727	20.822	46.554			
4800	10.000	30.938	21.031	47.554			
4900	10.000	31.144	21.235	48.554			
4965	10.000	31.276	21.366	49.204			
4965	12.401	59.735	21.366	190.501			
5000	12.500	59.822	21.635	190.936			
5100	12.775	60.072	22.386	192.200			
5200	13.033	60.322	23.112	193.491			
5300	13.275	60.573	23.817	194.806			
5400	13.498	60.823	24.500	196.145			
5500	13.703	61.073	25.163	197.505			
5600	13.889	61.321	25.806	198.885			
5700	14.056	61.569	26.432	200.283			
5800	14.204	61.815	27.040	201.696			
5900	14.334	62.058	27.630	203.123			
6000	14.444	62.300	28.206	204.562			

MOLYBDENUM REFERENCE STATE

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	cal/°K gfw			Kcal/gfw			
	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	± .300	± .100	± .100	± .000			
1000	± .500	± .600	± .320	± .280			
2000	± .800	± 1.050	± .580	± .930			
2890	± 2.000	± 1.570	± .820	± 2.180			
2890	± 2.000	± 1.920	± .820	± 3.180			
3000	± 2.000	± 1.990	± .860	± 3.400			
4000	± 3.000	± 2.710	± 1.240	± 5.900			
4965	± 4.000	± 3.470	± 1.600	± 9.270			
4965	± .004	± .003					
5000	± .004	± .003					
6000	± .005	± .004					

1) Heat capacity

Heat capacity values reported near room temperature ranged from 5.6[139] to 6.3[173] with most values near 5.7.[268, 270, 274, 275, 27(
The uncertainty in C_p° at 298.15 °K was therefore taken to be ±0.3 cal/° K g atom. Comparison of reported values in a graphical fashion at 1000° K[277] indicated an uncertainty of ± 0.5 cal/° K g atom. A similar comparison at 2000 °K led to an uncertainty of ± 0.8 cal/° K g atom. From 2000 °K to the melting point, the data of Rasor and McClelland[27, 157] showed a rather rapid rise with temperature while the data of Kothen[266] showed an almost linear rise with temperature. The uncertainty may therefore be as large as 2.0 cal/° K g atom at the melting point of 2890 °K.

The heat capacity of liquid molybdenum had apparently never been experimentally measured; therefore, a rather large overall uncertainty was arbitrarily assigned to it. Particular uncertainties assigned were as follows:

± 2.0 cal/° K g atom at m.p. (2890 °K)

± 2.0 cal/° K g atom at 3000 °K

± 3.0 cal/° K g atom at 4000 °K

± 4.0 cal/° K g atom at b.p. (4965 °K).

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[268] Bronson, H.L. and H.M. Chisholm, Proc. Nova Scotia Inst. Sci. 17, 44 (1929).

[269] Bronson, H.L., H.M. Chisholm, and S.M. Dockerty, Can. J. Res. 8, 282 (1933).

[270] Cooper, D. and G.O. Langstroth, Phys. Rev., 33, 243 (1929).

[271] Defacqz, E. and M. Guichard, Ann. Chim. Phys. 24, 139 (1901).

[272] Jaeger, F.M. and W.A. Veenstra, Proc. Acad. Sci. (Amsterdam) 37, 61 (1934).

[273] Jaeger, F.M. and W.A. Veenstra, Rec. Trav. Chim. 58, 677 (1934).

[274] Stern, T.E., Phys. Rev. 32, 298 (1928).

[275] Fieldhouse, I., J. Hedge, J. Lange, A. Takata, and T. Waterman, Tech. Rep. 55-495, WADC (3 August 1956).

[276] Simon, F. and W. Zeidler, Z. Physik. Chem. 133, 383 (1926).

[277] Goldsmith, A., T.E. Waterman, and H.G. Hirschhorn, Thermophysical Properties of Solid Materials, vol. I, Elements, TR-58-476, WADC (January 1960).

2) Entropy

Uncertainties in entropy values were calculated from assigned uncertainties in C_p° values (assuming that uncertainties in C_p° were not functions of temperature and using average uncertainties over a temperature range) and assigned values of uncertainties for ΔH's of transitions. The equations employed were as follows:

a) For single-phase regions

$$s_{T_2} = s_{T_1} + \delta C_p \ln \frac{T_2}{T_1} , \qquad (148)$$

where

s_{T_2} = entropy uncertainty at T_2,

s_{T_1} = entropy uncertainty at T_1,

δC_p° = average uncertainty in C_p° over the temperature range $T_1 < T < T_2$.

b) At transitions

$$s_B = s_A + \frac{\delta \Delta H_t}{T_t} , \qquad (149)$$

where

s_B = entropy uncertainty for phase B at temperature of transition T_t,

s_A = entropy uncertainty for phase A at temperature of transition T_t,

$\delta \Delta H_t$ = uncertainty in ΔH of transition.

The uncertainty in S_{298}° was taken to be $\pm$ 0.1 e.u. in view of the rather large uncertainty in C_p° near room temperature.

3) Enthalpy

Uncertainties in enthalpy values were calculated from C_p° uncertainties and assigned values of ΔH-of-transition uncertainties. The equations used for single-phase regions and transitions were

$$h_{T_2} = h_{T_1} + \delta C_p^\circ (T_2 - T_1) \tag{150}$$

and

$$h_B = h_A + \delta \Delta H_t \quad . \tag{151}$$

4) Free energy

The uncertainty in the free energy function was calculated from calculated uncertainties in S_T° and $H_T^\circ - H_{298}^\circ$ by means of equations (119) and (120).

g. Uncertainty in Gas Phase Functions

Uncertainties in the thermodynamic functions at the specified temperatures were computed as explained in section III-D2. They are summarized on the back of Table XXIX.

The uncertainties in ΔH_f° , ΔF_f° , and $\log_{10} K_p$ were calculated by means of equations (46), (47) and (48).

h. Other References Pertaining to Thermodynamics of Molybdenum

Heat capacity measurements at low temperatures have been reported and discussed by Boosz,[278] Wolcott,[204] Rayne,[279] Horowitz and Daunt,[280] and Simon and Zeidler.[276] Recent work on heat capacities at higher temperatures has been that of Boggs and Wiebelt.[281]

Vapor pressure data have also been reported by van Liempt.[282]

Useful annotated bibliographies on molybdenum were those of Goodwin,[209]

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[278] Boosz, H.J. Metall. 11, 22 (1957).

[279] Rayne, J.A., Phys. Rev. 95, 1428 (1954).

[280] Horowitz, M. and J.G. Daunt, Phys. Rev. 91, 1099 (1953).

[281] Boggs, J.H. and J.A. Wiebelt, Rept. AECU-4473, U.S. Atomic Energy Commission (November 1959).

[282] van Liempt, J.A.M., Z. Anorg. u. Allgem. Chem. 114, 105 (1920).

and of Richert, Beckett, and Johnston.[283] A recent review article of Argent and Milne[284] was examined but not used, since it did not provide any new data.

i. Thermodynamic Functions

The reference state thermodynamic functions of molybdenum are given in Table XXVIII. The ideal monatomic gas thermodynamic functions of molybdenum in Table XXIX were calculated using the energy levels given by Moore.[52] $H^\circ_{298} - H^\circ_0$ was found to be 1,481 cal/mole for the ideal gas.

[283] Richert, E., C.W. Beckett, and H.L.Johnston, Cryogenic Lab., Ohio State Univ. Tech. Rept. No. 102-AC49/12-100, Astia No. ATI 111-799 (1949).

[284] Argent, B.B. and C.J.C. Milne, J. Less Common Metals 2, 154 (1960).

TABLE XXIX

MOLYBDENUM — IDEAL MONATOMIC GAS — Mo

Reference State for Calculating ΔH_f°, ΔF_f°, and $\text{Log } K_p$: Solid from 298.15° to 2890°K, Liquid from 2890° to 4965°K, Gas from 4965° to 6000°K.

gfw = 95.95 — m.p. = 2890° ± 10°K — b.p. = 4965° ± 300°K

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-1.481	157.811	157.811	Infinite
298.15	4.968	43.462	43.462	0.000	158.200	147.278	-107.953
300	4.968	43.493	43.463	0.009	158.198	147.210	-107.237
400	4.968	44.922	43.657	0.506	158.111	143.560	-78.434
500	4.968	46.031	44.025	1.003	158.000	139.937	-61.163
600	4.968	46.937	44.437	1.500	157.875	136.334	-49.657
700	4.968	47.703	44.851	1.996	157.736	132.754	-41.446
800	4.968	48.366	45.249	2.493	157.593	129.195	-35.293
900	4.968	48.951	45.629	2.990	157.440	125.654	-30.512
1000	4.968	49.475	45.988	3.487	157.277	122.131	-26.690
1100	4.969	49.948	46.327	3.984	157.094	118.624	-23.567
1200	4.970	50.381	46.647	4.481	156.891	115.136	-20.968
1300	4.972	50.778	46.949	4.978	156.668	111.666	-18.772
1400	4.977	51.147	47.236	5.475	156.425	108.213	-16.892
1500	4.985	51.491	47.509	5.973	156.173	104.778	-15.265
1600	4.998	51.813	47.768	6.472	155.892	101.362	-13.845
1700	5.017	52.116	48.015	6.973	155.586	97.961	-12.593
1800	5.043	52.404	48.251	7.476	155.255	94.581	-11.483
1900	5.079	52.677	48.476	7.982	154.897	91.221	-10.492
2000	5.125	52.939	48.693	8.492	154.512	87.878	-9.602
2100	5.183	53.190	48.901	9.007	154.099	84.557	-8.799
2200	5.255	53.433	49.102	9.529	153.658	81.299	-8.076
2300	5.340	53.669	49.295	10.059	153.189	77.977	-7.409
2400	5.440	53.898	49.482	10.598	152.691	74.717	-6.804
2500	5.556	54.122	49.663	11.147	152.162	71.480	-6.327
2600	5.689	54.343	49.839	11.710	151.605	68.260	-5.738
2700	5.839	54.560	50.010	12.286	151.018	65.067	-5.267
2800	6.006	54.776	50.176	12.878	150.402	61.897	-4.831
2890	6.171	54.968	50.323	13.426	149.822	59.057	-4.466
2890	6.171	54.968	50.323	13.426	143.172	59.057	-4.466
2900	6.190	54.989	50.339	13.487	143.133	58.771	-4.429
3000	6.392	55.203	50.497	14.116	142.762	55.869	-4.070
3100	6.611	55.416	50.652	14.766	142.412	52.979	-3.735
3200	6.847	55.629	50.805	15.439	142.085	50.096	-3.421
3300	7.099	55.844	50.954	16.136	141.782	47.226	-3.128
3400	7.367	56.060	51.101	16.860	141.506	44.363	-2.852
3500	7.650	56.277	51.246	17.610	141.256	41.510	-2.592
3600	7.946	56.497	51.389	18.390	141.036	38.664	-2.347
3700	8.254	56.719	51.530	19.200	140.846	35.827	-2.116
3800	8.573	56.943	51.669	20.041	140.687	32.992	-1.897
3900	8.901	57.170	51.807	20.915	140.561	30.155	-1.690
4000	9.235	57.400	51.944	21.822	140.468	27.328	-1.493
4100	9.575	57.632	52.080	22.762	140.408	24.498	-1.306
4200	9.917	57.867	52.215	23.736	140.382	21.672	-1.128
4300	10.260	58.104	52.349	24.745	140.391	18.851	-0.958
4400	10.601	58.344	52.483	25.788	140.434	16.020	-0.796
4500	10.939	58.586	52.616	26.865	140.511	13.190	-0.641
4600	11.271	58.830	52.748	27.976	140.622	10.359	-0.492
4700	11.595	59.076	52.880	29.119	140.765	7.529	-0.350
4800	11.909	59.323	53.012	30.295	140.941	4.690	-0.214
4900	12.211	59.572	53.143	31.501	141.147	1.852	-0.083
4965	12.401	59.735	53.229	32.301	141.297	0.000	0.000
4965	12.401	59.735	53.229	32.301			
5000	12.500	59.822	53.274	32.736			
5100	12.775	60.072	53.405	34.000			
5200	13.033	60.322	53.536	35.291			
5300	13.275	60.573	53.666	36.606			
5400	13.498	60.823	53.796	37.945			
5500	13.703	61.073	53.926	39.305			
5600	13.889	61.321	54.056	40.685			
5700	14.056	61.569	54.186	42.083			
5800	14.204	61.815	54.315	43.496			
5900	14.334	62.058	54.444	44.923			
6000	14.444	62.300	54.573	46.362			

MOLYBDENUM IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	cal/°K gfw			Kcal/gfw			Log K_p
	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	
298.15	±.000	±.002	±.002	±.000	± .800	± .830	±.610
1000	±.000	±.002	±.002	±.000	±1.080	±1.120	±.240
2000	±.000	±.002	±.003	±.000	±1.730	±1.970	±.220
2800	±.001	±.003	±.003	±.001	±2.980	±3.180	±.240
2890	±.001	±.003	±.003	±.001	±3.980	±3.180	±.240
3000	±.001	±.003	±.003	±.001	±4.200	±3.390	±.250
4000	±.002	±.003	±.003	±.002	±6.700	±5.770	±.320
4965	±.004	±.003	±.003	±.004	±10.070	±8.760	±.390
4965	±.004	±.003	±.003	±.004			
5000	±.004	±.003	±.003	±.004			
6000	±.005	±.004	±.003	±.008			

gfw = 92.91

T, °K	cal/°K gfw C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	Kcal/gfw $H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite				
298.15	7.208	44.492	44.492	0.000			
300	7.208	44.537	44.492	0.013			
400	7.086	46.597	44.774	0.729			
500	6.893	48.157	45.301	1.428			
600	6.704	49.397	45.884	2.108			
700	6.541	50.418	46.461	2.770			
800	6.402	51.282	47.001	3.417			
900	6.285	52.029	47.528	4.051			
1000	6.186	52.686	48.012	4.674			
1100	6.103	53.272	48.464	5.289			
1200	6.035	53.800	48.887	5.895			
1300	5.981	54.280	49.283	6.496			
1400	5.941	54.722	49.656	7.092			
1500	5.915	55.131	50.008	7.685			
1600	5.903	55.512	50.340	8.276			
1700	5.904	55.870	50.655	8.866			
1800	5.918	56.208	50.954	9.457			
1900	5.945	56.528	51.239	10.050			
2000	5.984	56.834	51.511	10.646			
2100	6.034	57.127	51.772	11.247			
2200	6.094	57.409	52.022	11.853			
2300	6.164	57.682	52.262	12.466			
2400	6.242	57.946	52.493	13.086			
2500	6.328	58.202	52.716	13.715			
2600	6.419	58.452	52.932	14.352			
2700	6.516	58.696	53.141	14.999			
2800	6.616	58.935	53.344	15.655			
2900	6.719	59.169	53.541	16.322			
3000	6.825	59.399	53.732	16.999			
3100	6.931	59.624	53.919	17.687			
3200	7.038	59.846	54.100	18.385			
3300	7.144	60.064	54.278	19.095			
3400	7.250	60.279	54.451	19.814			
3500	7.354	60.491	54.621	20.545			
3600	7.456	60.699	54.787	21.285			
3700	7.555	60.905	54.949	22.036			
3800	7.652	61.108	55.109	22.796			
3900	7.747	61.308	55.265	23.566			
4000	7.838	61.505	55.419	24.345			
4100	7.926	61.700	55.569	25.133			
4200	8.011	61.892	55.718	25.930			
4300	8.093	62.081	55.863	26.736			
4400	8.172	62.268	56.007	27.549			
4500	8.247	62.453	56.148	28.370			
4600	8.320	62.635	56.287	29.198			
4700	8.390	62.814	56.424	30.034			
4800	8.456	62.992	56.559	30.876			
4900	8.520	63.167	56.692	31.725			
5000	8.581	63.339	56.823	32.580			
5100	8.640	63.510	56.953	33.441			
5200	8.695	63.678	57.081	34.308			
5300	8.749	63.844	57.207	35.180			
5400	8.800	64.008	57.331	36.057			
5500	8.848	64.170	57.454	36.940			
5600	8.895	64.330	57.575	37.827			
5700	8.939	64.488	57.695	38.719			
5800	8.981	64.644	57.814	39.615			
5900	9.021	64.798	57.931	40.515			
6000	9.059	64.950	58.046	41.419			

NIOBIUM IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal/gfw)	ΔH_f° (Kcal/gfw)	ΔF_f° (Kcal/gfw)	Log K_p
298.15	±.001	±.002	±.003	±.000			
1000	±.000	±.003	±.003	±.000			
2000	±.000	±.003	±.003	±.001			
3000	±.001	±.003	±.003	±.001			
4000	±.002	±.003	±.003	±.002			
5000	±.002	±.004	±.003	±.004			
6000	±.003	±.004	±.003	±.006			

11. Niobium

The ideal monatomic gas thermodynamic functions of niobium in Table XXX were calculated with the energy levels given by Moore[253] using the comp..ter program described in section III-D. Uncertainty estimates are summarized on the back of the table.

12. Nitrogen

a. Molecular Nitrogen

Machine computations based on the treatment of the diatomic molecule outlined in section III-E of this report, were made of the thermodynamic functions of molecular nitrogen .

The $\underline{X}\ {}^1\Sigma_g^+$ ground state and $\underline{A}\ {}^3\Sigma_u^+$ and $\underline{B}\ {}^3\Pi_g$ excited states of nitrogen were included in the calculation. The spectroscopic constants of Lofthus[285] were used for the ground state of N_2^{14}. He combined his observations of the near-ultraviolet part of the emission spectrum of nitrogen with the Raman spectrum results on nitrogen obtained by Stoicheff.[286] The resulting spectroscopic constants were slightly different from the ones listed by Herzberg.[54] Wilkinson and Houk[287] have also recently given constants for the ·ound state, which were later slightly modified by Wilkinson.[288] _ e constants listed by Herzberg[54] were used herein for the $\underline{A}$ and $\underline{B}$ states.

The spectroscopic constants adopted were corrected to correspond to the naturally occurring mixture of isotopic molecules although in the case of nitrogen, the resulting shift was less than the uncertainties assigned to the constants. According to custom for a process which does not involve separation of isotopes, the entropy of mixing of isotopes was not included. The entropy of nuclear spin was likewise omitted. No correction was necessary for the symmetry number of the heteronuclear isotopic molecule $N^{14}N^{15}$ since this correction has been shown to be unnecessary by Giauque and Overstreet.[289]

The effect of the presence of isotopic molecules was accounted for by the use of the average molecular weight on the chemical scale in the calculation of translational entropy and the use of averages of the spectroscopic constants of the isotopes weighted according to composition. The procedure given by Herzberg[54] was used to calculate the spectroscopic constants of $N^{15}N^{15}$ and $N^{14}N^{15}$ from those of $N^{14}N^{14}$.

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[285] Lofthus, A., Can. J. Phys. 34, 780 (1956).

[286] Stoicheff, B. P., Can. J. Phys. 32, 630 (1954).

[287] Wilkinson, P. G. and N. B. Houk, J. Chem. Phys. 24, 528 (1956).

[288] Wilkinson, P. G., Astrophys. J. 126, 1 (1957).

[289] Giauque, W. F. and R. Overstreet, J. Am. Chem. Soc. 54, 1731 (1932).

For discussion purposes, the properties of an isotopic molecule differing from those of the ordinary molecule are designated by the superscript i . If the parameter ρ is defined as

$$\rho = \sqrt{\mu/\mu^i} , \tag{152}$$

where μ is the reduced mass, then to a good approximation, the spectroscopic constants are related by equations (153)

$$\omega_e^i = \rho\omega_e , \; \omega_e^i x_e^i = \rho^2 \omega_e x_e , \; \omega_e^i y_e^i = \rho^3 \omega_e y_e , \; B_e^i = \rho^2 B_e ,$$

$$\alpha_e^i = \rho^3 \alpha_e , \text{ and } D_e^i = \rho^4 D_e . \tag{153}$$

The values of ρ for the pairs $N^{14}N^{14}$, $N^{14}N^{15}$ and $N^{14}N^{14}$, $N^{15}N^{15}$ were 0.983243 and 0.966195, respectively, using the isotopic masses tabulated by Stehn and Clancy.[290] The fractions of $N^{14}N^{14}$, $N^{14}N^{15}$, and $N^{15}N^{15}$ in naturally occurring molecular nitrogen were calculated from the isotopic abundances[291] by assuming that the equilibrium constant for the exchange process,

$$N^{14}N^{14} + N^{15}N^{15} \rightleftharpoons 2N^{14}N^{15} , \tag{154}$$

equaled 4; i.e., the distribution among the isotopic species was random.

The corrected spectroscopic constants and the assigned uncertainties (in cm^{-1}) which were used in the machine computations were as follows:

State	E	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_e	$y_e \times 10^5$	$D_e \times 10^6$
$X\ ^1\Sigma_g^+$	0.0	2357.93 ± 0.4	14.186 ± 0.12	-0.0124 ± 0.008	1.9981 ±0.001	0.01709 ±0.001	-4.6 ± 2.0	6 ± 0.5
$A\ ^3\Sigma_u^+$	49757.2 ± 2.0	1460.19 ± 0.5	13.888	-0.025	1.440	0.013	---	5.6
$B\ ^3\Pi_g$	59314.2 ± 2.0	1733.89 ± 0.5	14.47	---	1.6376	0.0184	---	5.8

[290] Lange, N. (ed.), Handbook of Chemistry, 9th ed., Handbook Publ., Sandusky, Ohio (1956), p 113.

[291] Strominger, D. J. M. Hollander and G. T. Seaborg, Rev. Mod. Phys. 30, 585 (1958).

The calculated thermodynamic functions of molecular nitrogen are given in Table XXXI. The indicated uncertainties in the spectroscopic constants made a difference of 0.0005 units in the entropy at 6000° K. The uncertainty estimates summarized on the back of the table reflect primarily the uncertainty in the value of the gas constant R.

No attempt was made to assess the uncertainties introduced by the approximations made here in the evaluation of the partition function of the diatomic molecule. However, values of the heat content and free-energy functions from the present calculation are compared immediately below at several temperatures with data from other sources to give an indication of the effect of the approximations.

Temp. ° K	$(H^\circ_T - H^\circ_{298})$ Kcal/gfw			$-(F^\circ_T - H^\circ_{298})/T$ cal/°K gfw		
	Avco	NBS[a]	JANAF[b]	Avco	NBS[a]	JANAF[b]
298.15	0.000	0.000	0.000	45.771	45.763	45.770
1000	5.130	5.130	5.129	49.380	49.373	49.378
2000	13.418	13.418	13.418	53.515	53.508	53.513
3000	22.160	22.159	22.165	56.378	56.372	56.376
4000	31.075	31.080	31.089	58.560	58.554	58.559
5000	40.089	40.098	40.119	60.322	60.316	60.322
6000	49.179	---	49.237	61.801	---	61.802

[a]Re-calculated from National Bureau of Standards values in Circ. 564 to a reference temperature of 298.15° K.

[b]From JANAF Thermochemical Tables (31 March 1961). ("White sheet") provided in advance of publication through the courtesy of Dr. D. R. Stull.)

The NBS table was based largely on calculations of Goff and Gratch[292] (60° to 2800° K) and was extended to 5000° K by NBS using the same spectroscopic data. The spectroscopic data used were essentially those listed by Herzberg[54] except for somewhat smaller values of B_e and α_e. The JANAF table was a modification of the calculations of

[292]Goff, J. A. and S. Gratch, Trans. Am. Soc. Mech. Engrs. 72, 741 (1950).

TABLE XXXI

NITROGEN — REFERENCE STATE — N_2

Reference State for Calculating ΔH_f°, ΔF_f°, and $\text{Log } K_p$:
Diatomic Gas from 298.15° to 6000°K.

gfw = 28.016

T, °K	cal/°K gfw C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	Kcal/gfw $H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	$\text{Log } K_p$
0	0.000	0.000	Infinite	-2.072			
298.15	6.961	45.771	45.771	0.000			
300	6.961	45.814	45.771	0.013			
400	6.991	47.820	46.045	0.710			
500	7.070	49.388	46.562	1.413			
600	7.197	50.687	47.144	2.126			
700	7.351	51.808	47.732	2.853			
800	7.513	52.800	48.305	3.596			
900	7.670	53.695	48.855	4.356			
1000	7.815	54.510	49.380	5.130			
1100	7.945	55.261	49.881	5.918			
1200	8.061	55.958	50.359	6.719			
1300	8.162	56.607	50.815	7.530			
1400	8.250	57.215	51.251	8.351			
1500	8.328	57.787	51.667	9.180			
1600	8.396	58.327	52.067	10.016			
1700	8.456	58.838	52.450	10.858			
1800	8.509	59.322	52.819	11.707			
1900	8.555	59.784	53.173	12.560			
2000	8.597	60.224	53.515	13.418			
2100	8.635	60.644	53.844	14.279			
2200	8.668	61.047	54.163	15.144			
2300	8.698	61.433	54.471	16.013			
2400	8.726	61.803	54.768	16.884			
2500	8.751	62.160	55.057	17.758			
2600	8.774	62.504	55.337	18.634			
2700	8.795	62.835	55.608	19.513			
2800	8.814	63.156	55.872	20.393			
2900	8.832	63.465	56.129	21.276			
3000	8.849	63.765	56.378	22.160			
3100	8.865	64.055	56.621	23.045			
3200	8.879	64.337	56.858	23.933			
3300	8.893	64.610	57.089	24.821			
3400	8.906	64.876	57.314	25.711			
3500	8.918	65.134	57.534	26.602			
3600	8.930	65.386	57.748	27.495			
3700	8.941	65.631	57.958	28.388			
3800	8.951	65.869	58.163	29.283			
3900	8.961	66.102	58.364	30.178			
4000	8.971	66.329	58.560	31.075			
4100	8.980	66.551	58.752	31.973			
4200	8.989	66.767	58.941	32.871			
4300	8.998	66.979	59.125	33.770			
4400	9.006	67.186	59.306	34.671			
4500	9.014	67.388	59.483	35.572			
4600	9.022	67.587	59.657	36.474			
4700	9.030	67.781	59.828	37.376			
4800	9.038	67.971	59.996	38.280			
4900	9.045	68.157	60.161	39.184			
5000	9.053	68.340	60.322	40.089			
5100	9.060	68.520	60.481	40.994			
5200	9.068	68.696	60.638	41.901			
5300	9.075	68.868	60.792	42.808			
5400	9.083	69.038	60.943	43.716			
5500	9.090	69.205	61.091	44.624			
5600	9.098	69.369	61.238	45.534			
5700	9.105	69.530	61.382	46.444			
5800	9.113	69.689	61.524	47.355			
5900	9.122	69.844	61.664	48.267			
6000	9.130	69.998	61.801	49.179			

NITROGEN REFERENCE STATE

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	cal/°K gfw			Kcal/gfw			Log K_p
	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	
298.15	±.000	±.002	±.002	±.000			
1000	±.000	±.003	±.002	±.000			
2000	±.000	±.003	±.003	±.001			
3000	±.000	±.004	±.003	±.001			
4000	±.000	±.004	±.003	±.001			
5000	±.000	±.004	±.003	±.001			
6000	±.000	±.004	±.003	±.001			

TABLE XXXII

NITROGEN | IDEAL MONATOMIC GAS | N

Reference State for Calculating ΔH_f°, ΔF_f°, and $\text{Log } K_p$:
Diatomic Gas from 298.15° to 6000°K.

gfw = 14.008

T, °K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal/gfw)	ΔH_f° (Kcal/gfw)	ΔF_f° (Kcal/gfw)	Log K_p
0	0.000	0.000	Infinite	-1.481	112.536	112.536	Infinite
298.15	4.968	36.615	36.615	0.000	112.980	108.887	-79.812
300	4.968	36.645	36.615	0.009	112.983	108.861	-79.301
400	4.968	38.074	36.809	0.506	113.131	107.465	-58.713
500	4.968	39.183	37.177	1.003	113.277	106.032	-46.344
600	4.968	40.089	37.590	1.500	113.417	104.569	-38.087
700	4.968	40.855	38.003	1.996	113.550	103.084	-32.183
800	4.968	41.518	38.402	2.493	113.675	101.580	-27.749
900	4.968	42.103	38.781	2.990	113.792	100.061	-24.297
1000	4.968	42.627	39.140	3.487	113.902	98.530	-21.533
1100	4.968	43.100	39.479	3.984	114.005	96.987	-19.269
1200	4.968	43.533	39.799	4.481	114.101	95.437	-17.381
1300	4.968	43.930	40.101	4.977	114.192	93.879	-15.782
1400	4.968	44.298	40.388	5.474	114.278	92.312	-14.410
1500	4.968	44.641	40.661	5.971	114.361	90.740	-13.220
1600	4.968	44.962	40.919	6.468	114.440	89.164	-12.179
1700	4.968	45.263	41.166	6.965	114.516	87.580	-11.259
1800	4.968	45.547	41.402	7.461	114.587	85.993	-10.440
1900	4.969	45.816	41.627	7.958	114.658	84.402	-9.708
2000	4.969	46.070	41.843	8.455	114.726	82.810	-9.049
2100	4.970	46.313	42.050	8.952	114.792	81.211	-8.451
2200	4.971	46.544	42.249	9.449	114.857	79.610	-7.908
2300	4.972	46.765	42.441	9.946	114.920	78.006	-7.412
2400	4.975	46.977	42.625	10.444	114.982	76.402	-6.957
2500	4.978	47.180	42.803	10.941	115.042	74.792	-6.538
2600	4.982	47.375	42.976	11.439	115.102	73.179	-6.151
2700	4.987	47.563	43.142	11.938	115.162	71.567	-5.793
2800	4.993	47.745	43.303	12.437	115.221	69.952	-5.460
2900	5.00[illegible]	47.920	43.459	12.936	115.278	68.334	-5.150
3000	5.010	48.090	43.611	13.437	115.337	66.714	-4.860
3100	5.022	48.254	43.758	13.938	115.397	65.091	-4.589
3200	5.035	48.414	43.901	14.441	115.455	63.469	-4.335
3300	5.050	48.569	44.040	14.945	115.515	61.843	-4.095
3400	5.066	48.720	44.176	15.451	115.575	60.215	-3.870
3500	5.085	48.867	44.308	15.959	115.638	58.584	-3.658
3600	5.107	49.011	44.436	16.468	115.700	56.956	-3.458
3700	5.130	49.151	44.562	16.980	115.766	55.323	-3.268
3800	5.155	49.288	44.684	17.494	115.833	53.691	-3.088
3900	5.183	49.422	44.804	18.011	115.902	52.054	-2.917
4000	5.213	49.554	44.921	18.531	115.973	50.416	-2.754
4100	5.244	49.683	45.036	19.054	116.048	48.774	-2.600
4200	5.278	49.810	45.148	19.580	116.124	47.132	-2.452
4300	5.314	49.935	45.258	20.110	116.205	45.487	-2.312
4400	5.351	50.057	45.366	20.643	116.287	43.843	-2.178
4500	5.390	50.178	45.471	21.180	116.374	42.195	-2.049
4600	5.431	50.297	45.575	21.721	116.465	40.544	-1.926
4700	5.473	50.414	45.676	22.266	116.558	38.899	-1.809
4800	5.517	50.530	45.776	22.816	116.656	37.246	-1.696
4900	5.562	50.644	45.875	23.369	116.758	35.584	-1.587
5000	5.608	50.757	45.971	23.928	116.864	33.930	-1.483
5100	5.654	50.868	46.066	24.491	116.974	32.267	-1.383
5200	5.702	50.978	46.159	25.059	117.089	30.607	-1.286
5300	5.751	51.088	46.251	25.632	117.208	28.948	-1.194
5400	5.800	51.195	46.342	26.209	117.332	27.277	-1.104
5500	5.850	51.302	46.431	26.792	117.460	25.612	-1.018
5600	5.899	51.408	46.519	27.379	117.592	23.940	-0.934
5700	5.950	51.513	46.606	27.971	117.730	22.266	-0.854
5800	6.000	51.617	46.691	28.569	117.872	20.592	-0.776
5900	6.050	51.720	46.776	29.171	118.019	18.910	-0.700
6000	6.100	51.822	46.859	29.779	118.170	17.226	-0.6[illegible]

NITROGEN IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	±.000	±.002	±.002	±.000	±.100	±.100	±.070
1000	±.000	±.002	±.002	±.000	±.100	±.100	±.020
2000	±.000	±.002	±.002	±.000	±.100	±.110	±.010
3000	±.000	±.002	±.002	±.001	±.100	±.110	±.010
4000	±.000	±.002	±.002	±.001	±.100	±.120	±.005
5000	±.001	±.002	±.002	±.001	±.100	±.120	±.005
6000	±.001	±.002	±.003	±.002	±.100	±.130	±.005

Glatt, Belzer, and Johnston,[293] who had used the spectroscopic data given by Herzberg.[54] The modifications in the JANAF tables were the addition of -Rln 9 to the entropy to remove the effect of nuclear spin included by Glatt, Belzer, and Johnston[293] and 0.012 e.u. to convert to the spectroscopic data of Stoicheff.[286] The vibrational constants used herein for the ground state were slightly different from those given by Stoicheff,[286] but that difference was within the uncertainties summarized above.

$(H^\circ_{298} - H^\circ_0)$ for molecular nitrogen was calculated to be 2072.3 cal/gfw.

b. Monatomic Nitrogen

1) Dissociation energy of nitrogen

The dissociation energy of molecular nitrogen was a subject of dispute for many years. A set of possible values resulted from differences between the dissociation limits obtained from the predissociation of various excited states, particularly the $C\ ^3\Pi_g$ state, and the energies of various combinations of three possible low-lying states of the atomic dissociation products.[3] From this set, the alternative values of 9.76 and 7.38 ev appeared most likely, and a great amount of work has been done to confirm one or the other value. The subject was reviewed by Gaydon[294] in 1953, and by Brewer and Searcy[295] in 1956. Several other papers[285,287,296-300] have appeared since Brewer and Searcy's review. There has been achieved a virtually unanimous agreement that the higher value is correct. The dissociation energy of N_2^{14} was therefore taken to be 225.07 ± 0.1 Kcal/gfw from Brewer and Searcy's recommended value of 78717 ± 40 cm^{-1} (1 cm^{-1} = 2.85927 cal/gfw). The correction to convert this to the naturally occurring isotopic mixture is negligible.[294]

2) Thermodynamic functions of monatomic nitrogen

The ideal gas thermodynamic functions in Table XXXII were calculated with the energy levels given by Moore[52] and the computer program discussed in section III-D. Uncertainty estimates are summarized on the back of the table. $H^\circ_{298} - H^\circ_0$ was found to be 1,481 cal/mole.

[293] Glatt, L., J. Belzer, and H. L. Johnston, Ohio State Univ. Research Found., Proj. 316, Rep. 9 (1953).

[294] Gaydon, A. G., Dissociation Energies and Spectra of Diatomic Molecules, 2nd ed., Rev., Chapman and Hall, London (1953).

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13. Osmium

The ideal monatomic gas thermodynamic functions of osmium in Table XXXIII were calculated from the energy levels given by Moore[221] with the computer program discussed in section III-D. Uncertainty estimates are summarized on the back of the table.

TABLE XXXIII

OSMIUM — IDEAL MONATOMIC GAS — Os

gfw = 190.2

T, °K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal/gfw)	ΔH_f° (Kcal/gfw)	ΔF_f° (Kcal/gfw)	Log K_p
0	0.000	0.000	Infinite				Infinite
298.15	4.968	46.002	46.002	0.000			
300	4.969	46.032	46.002	0.009			
400	4.974	47.462	46.197	0.506			
500	4.996	48.574	46.565	1.005			
600	5.044	49.489	46.978	1.506			
700	5.122	50.272	47.394	2.014			
800	5.231	50.962	47.798	2.532			
900	5.367	51.586	48.185	3.061			
1000	5.522	52.159	48.554	3.606			
1100	5.691	52.694	48.906	4.166			
1200	5.867	53.196	49.243	4.744			
1300	6.042	53.673	49.565	5.340			
1400	6.211	54.127	49.875	5.952			
1500	6.372	54.561	50.173	6.582			
1600	6.521	54.977	50.460	7.226			
1700	6.658	55.376	50.738	7.885			
1800	6.782	55.761	51.006	8.558			
1900	6.895	56.130	51.266	9.241			
2000	6.998	56.487	51.519	9.936			
2100	7.091	56.830	51.765	10.641			
2200	7.177	57.162	52.001	11.354			
2300	7.257	57.483	52.233	12.076			
2400	7.332	57.794	52.458	12.805			
2500	7.403	58.094	52.677	13.542			
2600	7.472	58.386	52.891	14.286			
2700	7.538	58.669	53.100	15.036			
2800	7.603	58.945	53.304	15.794			
2900	7.667	59.213	53.503	16.557			
3000	7.730	59.474	53.698	17.327			
3100	7.792	59.728	53.888	18.103			
3200	7.853	59.976	54.075	18.885			
3300	7.914	60.219	54.257	19.674			
3400	7.974	60.456	54.436	20.468			
3500	8.033	60.688	54.611	21.269			
3600	8.090	60.915	54.783	22.075			
3700	8.147	61.138	54.952	22.887			
3800	8.203	61.356	55.118	23.704			
3900	8.257	61.569	55.280	24.527			
4000	8.309	61.779	55.440	25.355			
4100	8.360	61.985	55.597	26.189			
4200	8.410	62.187	55.752	27.027			
4300	8.457	62.385	55.904	27.871			
4400	8.503	62.580	56.053	28.719			
4500	8.547	62.772	56.201	29.571			
4600	8.590	62.960	56.345	30.428			
4700	8.631	63.145	56.488	31.289			
4800	8.670	63.328	56.629	32.154			
4900	8.707	63.507	56.767	33.023			
5000	8.743	63.683	56.904	33.896			
5100	8.777	63.856	57.039	34.772			
5200	8.810	64.027	57.171	35.651			
5300	8.841	64.195	57.302	36.534			
5400	8.871	64.361	57.431	37.419			
5500	8.899	64.524	57.559	38.308			
5600	8.926	64.685	57.685	39.199			
5700	8.952	64.843	57.809	40.093			
5800	8.977	64.999	57.932	40.989			
5900	9.001	65.152	58.053	41.888			
6000	9.024	65.304	58.172	42.790			

OSMIUM IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	±.000	±.002	±.002	±.000			
1000	±.000	±.002	±.003	±.000			
2000	±.002	±.003	±.003	±.001			
3000	±.008	±.004	±.003	±.005			
4000	±.013	±.007	±.004	±.016			
5000	±.010	±.010	±.005	±.027			
6000	±.004	±.011	±.006	±.034			

14. Oxygen

a. Molecular Oxygen

The thermodynamic functions of molecular oxygen were calculated with a computer program based on the treatment of the diatomic molecule outlined in section III-E of this report.

The electronic states and spectroscopic constants used for the oxygen molecule are given below with the assigned uncertainties:

Constant	$X\ ^3\Sigma_g^-$	$a\ ^1\Delta_g$	$b\ ^1\Sigma_g^+$	$A\ ^3\Sigma_u^+$	$^1\Sigma_u^-$	$B\ ^3\Sigma_u^-$
E	- 0.244 $\pm$ 0.2	7882.36 $\pm$ 1.0	13120.917 $\pm$ 1.0	35008.0 $\pm$ 100.	36212.8 $\pm$1000.	49357.6 $\pm$ 10.
ω_e	1580.1622 $\pm$ 0.4	1509.1 $\pm$ 1.0	1432.507 $\pm$ 0.4	801.0	650.41	709.4
$\omega_e x_e$	12.07 $\pm$ 0.01	12.9 $\pm$ 0.4	13.9466 $\pm$ 0.02	15.0	17.03	8.0
$\omega_e y_e$	0.0546 $\pm$ 0.005	---	- 0.01075 $\pm$ 0.01	---	-0.106	-0.375
B_e	1.44531 $\pm$ 0.001	1.4260 $\pm$ 0.004	1.40007 $\pm$ 0.005	0.91	0.826	0.819
α_e	0.01579 $\pm$ 0.0001	0.0171 $\pm$ 0.006	0.01817 $\pm$ 0.0001	0.015	0.0205	0.011
γ_e ($\times 10^5$)	---	---	- 4.3 $\pm$ 4.0	---	-83.0	---
D_e ($\times 10^6$)	4.96 $\pm$ 0.1	5.1 $\pm$ 0.6	5.36 $\pm$ 0.5	3.4	5.3	4.4
g	3	2	1	3	7*	3

* Includes the $^3\Delta_u$ state on the assumption that its spectroscopic constants are the same as those of the $^1\Sigma_u^-$ state.

Constants adopted for O_2^{16} were converted to those appropriate to a naturally occurring isotopic mixture by the procedure discussed in section IV-A12, using data for the isotopic masses and abundances from the same sources.

Constants used for the X, a, and b states of O_2^{16} were those listed by Herzberg.[54] The rotation and vibration-rotation interaction constants of the ground state have received recent confirmation in the Raman spectroscopic results of Weber and McGinnis.[301] Woolley's[55] additive correction of -0.244 cm^{-1} was used to account for the effect of the triplet splitting of the ground state. Constants for the A state were from the modification of Herzberg's[302] results by Broida and Gaydon.[303]

Herzberg[304] reported two new states for molecular oxygen which have not been included in previous calculations of the thermodynamic functions. He gave constants for the $^1\Sigma_u^-$ state, which were adopted here, but noted that the constants were based on the assumption of a vibrational numbering which might have to be revised. Much less is known about the $^3\Delta_u$ state as the data are fragmentary. Moffit[305] had previously predicted the positions of these then unknown states, and concluded that they should be separated by less than 0.2 ev (1600 cm^{-1}) from the A state. Chamberlain[306] stated that the $^3\Delta_u$ state probably lies slightly above the A state. Later theoretical calculations relating to the $^1\Sigma_u^-$ and $^3\Delta_u$ states were discussed by Itoh and Kimio.[308] For the present calculation, the energies of the O-O bands of the two new states and their other spectroscopic constants were assumed identical. A total multiplicity of 7 was used. An uncertainty of 1000 cm^{-1} was assigned to the common electronic levels.

Spectroscopic constants for the B state were taken from Brix and Herzberg.[307]

The results of the computations of the thermodynamic functions of molecular oxygen are given in Table XXXIV. The entropies of isotopic mixing and nuclear spin were not included. The calculations of Woolley[55] have been almost universally accepted for recent compilations of thermodynamic functions.[77, 156, 309] Woolley[55] broke off summation of rotational levels for a given vibrational level at the top of the dissociation or pre-dissociation applying to the vibrational level. In the

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[301] Weber, A. and E. A. McGinnis, J. Mol. Spectroscopy 4, 195 (1960).

[302] Herzberg, G., Can. J. Phys. 30, 185 (1952).

[303] Broida, H. P. and A. G. Gaydon, Proc. Roy. Soc. (London) A222, 181 (1954).

[304] Herzberg, G., Can. J. Phys. 31, 657 (1953).

[305] Moffitt, W., Proc. Roy. Soc. (London) A210, 245 (1951).

[306] Chamberlain, J. W., Astrophys. J. 128, 713 (1958).

[307] Brix, P. and G. Herzberg, Can. J. Phys. 32, 110 (1954).

[308] Itoh, T. and O. Kimio, J. Chem. Phys. 25, 1098 (1956).

[309] Dergazarian et al, JANAF Thermochemical Tables, The Thermal Laboratory, Dow Chemical Co. (31 March 1961).

TABLE XXXIV

OXYGEN — REFERENCE STATE — O_2

Reference State for Calculating ΔH_f°, ΔF_f°, and Log K_p :
Diatomic Gas from 298.15° to 6000°K.

gfw = 32.000

T,°K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal/°K gfw			Kcal/gfw			
0	0.000	0.000	Infinite	-2.075			
298.15	7.021	49.007	49.007	0.000			
300	7.024	49.051	49.007	0.013			
400	7.196	51.092	49.284	0.723			
500	7.431	52.723	49.814	1.454			
600	7.670	54.099	50.417	2.210			
700	7.884	55.298	51.030	2.987			
800	8.064	56.363	51.631	3.785			
900	8.213	57.321	52.211	4.599			
1000	8.336	58.193	52.767	5.427			
1100	8.439	58.993	53.297	6.266			
1200	8.527	59.731	53.803	7.114			
1300	8.604	60.417	54.285	7.971			
1400	8.674	61.057	54.746	8.835			
1500	8.738	61.657	55.187	9.705			
1600	8.799	62.223	55.609	10.582			
1700	8.858	62.759	56.014	11.465			
1800	8.915	63.267	56.403	12.354			
1900	8.972	63.750	56.777	13.248			
2000	9.028	64.212	57.138	14.148			
2100	9.083	64.654	57.485	15.054			
2200	9.138	65.077	57.821	15.965			
2300	9.193	65.485	58.145	16.881			
2400	9.246	65.877	58.459	17.803			
2500	9.299	66.256	58.763	18.731			
2600	9.351	66.622	59.059	19.663			
2700	9.402	66.975	59.345	20.601			
2800	9.451	67.318	59.624	21.543			
2900	9.499	67.651	59.895	22.491			
3000	9.546	67.974	60.159	23.443			
3100	9.591	68.288	60.417	24.400			
3200	9.635	68.593	60.667	25.362			
3300	9.677	68.890	60.912	26.327			
3400	9.718	69.180	61.151	27.297			
3500	9.758	69.462	61.385	28.271			
3600	9.796	69.738	61.613	29.249			
3700	9.833	70.007	61.836	30.230			
3800	9.869	70.269	62.055	31.215			
3900	9.905	70.526	62.269	32.204			
4000	9.940	70.778	62.479	33.196			
4100	9.976	71.024	62.684	34.192			
4200	10.012	71.265	62.886	35.192			
4300	10.049	71.501	63.084	36.195			
4400	10.088	71.733	63.278	37.203			
4500	10.130	71.960	63.468	38.214			
4600	10.176	72.184	63.656	39.230			
4700	10.226	72.404	63.840	40.251			
4800	10.283	72.620	64.021	41.278			
4900	10.347	72.834	64.199	42.311			
5000	10.421	73.044	64.374	43.352			
5100	10.506	73.252	64.546	44.402			
5200	10.607	73.459	64.716	45.462			
5300	10.724	73.663	64.883	46.535			
5400	10.863	73.867	65.048	47.623			
5500	11.027	74.070	65.211	48.728			
5600	11.222	74.274	65.371	49.855			
5700	11.453	74.479	65.530	51.007			
5800	11.727	74.685	65.687	52.191			
5900	12.052	74.895	65.842	53.412			
6000	12.439	75.109	65.996	54.677			

OXYGEN REFERENCE STATE

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	cal/°K gfw C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	Kcal/gfw $H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	±.000	±.003	±.003	±.000			
1000	±.001	±.004	±.004	±.001			
2000	±.002	±.005	±.004	±.002			
3000	±.005	±.007	±.004	±.005			
4000	±.014	±.009	±.006	±.014			
5000	±.089	±.018	±.007	±.057			
6000	±.673	±.081	±.013	±.407			

present work, the sum has been taken to infinite energy. The effect of the alternative procedures will be evident only at the higher temperatures. Thus, at 5000°K, Woolley's[55] free-energy function would have been increased by 0.0003 cal/°K gfw had he summed to infinite energy, and his heat content would have been 14 cal/gfw greater. If levels for the two new states had been included, the differences in the two calculations for the free-energy function and heat content would have been 0.0005 cal/°K gfw and 30 cal/gfw, respectively, at 5000°K. Although some procedure for taking into account the effect of dissociation or pre-dissociation on the thermodynamic functions is certainly valid, it was preferred here to retain the simplicity of the present procedure. The uncertainty in the thermodynamic functions of oxygen which results is far less than the uncertainty in the functions of other substances with which the oxygen data will be combined. The uncertainties in the thermodynamic functions summarized on the back of Table XXXIV do not include a contribution from a summation to infinite energy.

The results of the present calculation are compared below with those in the JANAF compilation[309] at selected temperatures:

Temp. °K	$(H^\circ_T - H^\circ_{298})$ Kcal/gfw		$-(F^\circ_T - H^\circ_{298})/T$ cal/°K gfw	
	Avco	JANAF	Avco	JANAF
298.15	0.000	0.000	49.007	49.004
1000	5.427	5.427	52.767	52.765
2000	14.148	14.149	57.138	57.136
3000	23.443	23.446	60.159	60.157
4000	33.196	33.201	62.479	62.476
5000	43.352	43.257	64.374	64.368
6000	54.677	53.479	65.996	65.970

The JANAF table was taken from Woolley,[55] with a reduction of the entropies by 0.0065 cal/°K gfw. This amount had been added by Woolley[55] to account for the difference in symmetry number between heteronuclear and homonuclear isotopes.

$(H^\circ_{298} - H^\circ_0)$ was calculated to be 2074.7 cal/gfw.

b. Monatomic Oxygen

1) Dissociation energy of oxygen

The dissociation energy of O_2^{16} was taken to be 117.973 ± 0.04 Kcal/gfw (41260 ± 15 cm^{-1}) from Brix and Herzberg.[310] The correction to a naturally occurring isotopic mixture was negligible.

2) Ideal monatomic gas thermodynamic functions

The ideal monatomic gas thermodynamic functions of oxygen in Table XXXV were calculated with the energy levels given by Moore[52] and the computer program discussed in section III-D. Uncertainty estimates are summarized on the back of the table. $H^\circ_{298} - H^\circ_0$ was found to be 1,607.50 cal/mole for the ideal monatomic gas.

[310] Brix, P. and G. Herzberg, J. Chem. Phys. 21, 2240 (1953).

OXYGEN

TABLE XXXV

IDEAL MONATOMIC GAS

O

Reference State for Calculating ΔH_f°, ΔF_f°, and $\mathrm{Log}\ K_p$: Diatomic Gas from 298.15° to 6000° K.

gfw = 16.000

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-1.608	58.986	58.986	Infinite
298.15	5.237	38.469	38.469	0.000	59.557	55.393	-40.602
300	5.235	38.501	38.469	0.010	59.561	55.367	-40.333
400	5.135	39.992	38.673	0.528	59.724	53.945	-29.473
500	5.081	41.131	39.055	1.038	59.868	52.483	-22.939
600	5.049	42.054	39.480	1.544	59.996	50.994	-18.574
700	5.029	42.831	39.905	2.048	60.111	49.484	-15.449
800	5.015	43.502	40.314	2.550	60.214	47.959	-13.101
900	5.006	44.092	40.701	3.052	60.309	46.421	-11.272
1000	4.999	44.619	41.067	3.552	60.395	44.873	-9.806
1100	4.994	45.095	41.412	4.051	60.475	43.317	-8.606
1200	4.990	45.529	41.737	4.551	60.550	41.754	-7.604
1300	4.987	45.929	42.045	5.049	60.621	40.184	-6.755
1400	4.984	46.298	42.335	5.548	60.688	38.610	-6.027
1500	4.982	46.642	42.611	6.046	60.750	37.031	-5.395
1600	4.981	46.963	42.873	6.544	60.810	35.448	-4.842
1700	4.979	47.265	43.123	7.042	60.866	33.860	-4.353
1800	4.979	47.550	43.361	7.540	60.920	32.271	-3.918
1900	4.978	47.819	43.588	8.038	60.971	30.679	-3.529
2000	4.978	48.074	43.806	8.536	61.019	29.083	-3.178
2100	4.978	48.317	44.016	9.034	61.064	27.484	-2.860
2200	4.979	48.549	44.216	9.532	61.107	25.884	-2.571
2300	4.980	48.770	44.410	10.029	61.145	24.282	-2.307
2400	4.981	48.982	44.596	10.527	61.182	22.679	-2.065
2500	4.984	49.186	44.775	11.026	61.218	21.075	-1.842
2600	4.986	49.381	44.949	11.524	61.249	19.468	-1.636
2700	4.990	49.569	45.116	12.023	61.280	17.861	-1.446
2800	4.994	49.751	45.279	12.522	61.307	16.249	-1.268
2900	4.999	49.926	45.436	13.022	61.334	14.642	-1.103
3000	5.004	50.096	45.588	13.522	61.357	13.033	-0.949
3100	5.010	50.260	45.736	14.023	61.380	11.420	-0.805
3200	5.017	50.419	45.880	14.524	61.400	9.810	-0.670
3300	5.025	50.574	46.020	15.026	61.419	8.196	-0.543
3400	5.033	50.724	46.156	15.529	61.438	6.585	-0.423
3500	5.041	50.870	46.289	16.033	61.455	4.967	-0.310
3600	5.050	51.012	46.418	16.537	61.470	3.354	-0.204
3700	5.060	51.150	46.544	17.043	61.485	1.741	-0.103
3800	5.070	51.285	46.667	17.549	61.498	0.125	-0.007
3900	5.081	51.417	46.787	18.057	61.512	-1.490	0.083
4000	5.091	51.546	46.905	18.565	61.524	-3.107	0.170
4100	5.103	51.672	47.019	19.075	61.536	-4.719	0.252
4200	5.114	51.795	47.132	19.586	61.547	-6.337	0.330
4300	5.126	51.916	47.242	20.098	61.557	-7.953	0.404
4400	5.138	52.033	47.349	20.611	61.567	-9.567	0.475
4500	5.150	52.149	47.455	21.126	61.576	-11.188	0.543
4600	5.162	52.262	47.558	21.641	61.583	-12.801	0.608
4700	5.174	52.374	47.659	22.158	61.589	-14.416	0.670
4800	5.186	52.483	47.758	22.676	61.594	-16.033	0.730
4900	5.198	52.590	47.856	23.195	61.596	-17.652	0.787
5000	5.210	52.695	47.952	23.715	61.596	-19.268	0.842
5100	5.222	52.798	48.046	24.237	61.593	-20.885	0.895
5200	5.234	52.900	48.138	24.760	61.586	-22.499	0.946
5300	5.246	52.999	48.229	25.284	61.574	-24.114	0.994
5400	5.258	53.098	48.318	25.809	61.555	-25.731	1.041
5500	5.269	53.194	48.406	26.335	61.528	-27.348	1.087
5600	5.280	53.289	48.492	26.863	61.493	-28.957	1.130
5700	5.292	53.383	48.577	27.392	61.445	-30.571	1.172
5800	5.302	53.475	48.661	27.921	61.383	-32.182	1.213
5900	5.313	53.566	48.743	28.452	61.303	-33.793	1.252
6000	5.323	53.655	48.824	28.984	61.202	-35.399	1.289

OXYGEN IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	±.000	±.002	±.002	±.000	±.020	±.021	±.015
1000	±.000	±.002	±.002	±.000	±.021	±.024	±.005
2000	±.000	±.002	±.002	±.000	±.022	±.028	±.003
3000	±.000	±.002	±.002	±.000	±.025	±.032	±.002
4000	±.000	±.002	±.003	±.001	±.035	±.044	±.002
5000	±.000	±.002	±.003	±.001	±.078	±.053	±.002
6000	±.000	±.002	±.003	±.001	±.428	±.077	±.003

gfw = 195.09

T, °K	cal/°K gfw C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	Kcal. gfw $H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite				Infinite
298.15	6.102	45.962	45.962	0.000			
300	6.113	45.999	45.962	0.011			
400	6.459	47.817	46.207	0.644			
500	6.435	49.260	46.679	1.291			
600	6.260	50.419	47.209	1.926			
700	6.059	51.369	47.738	2.542			
800	5.877	52.166	48.243	3.138			
900	5.728	52.849	48.717	3.718			
1000	5.609	53.446	49.161	4.285			
1100	5.517	53.976	49.575	4.841			
1200	5.447	54.453	49.962	5.389			
1300	5.395	54.887	50.325	5.931			
1400	5.358	55.285	50.665	6.469			
1500	5.333	55.654	50.985	7.003			
1600	5.318	55.998	51.288	7.536			
1700	5.311	56.320	51.575	8.067			
1800	5.310	56.623	51.847	8.598			
1900	5.316	56.911	52.106	9.129			
2000	5.326	57.184	52.353	9.661			
2100	5.340	57.444	52.589	10.195			
2200	5.356	57.693	52.816	10.729			
2300	5.376	57.931	53.033	11.266			
2400	5.397	58.160	53.242	11.805			
2500	5.421	58.381	53.443	12.346			
2600	5.445	58.594	53.637	12.889			
2700	5.470	58.800	53.824	13.435			
2800	5.496	59.000	54.006	13.983			
2900	5.523	59.193	54.181	14.534			
3000	5.549	59.381	54.351	15.087			
3100	5.576	59.563	54.517	15.644			
3200	5.603	59.740	54.677	16.203			
3300	5.629	59.913	54.833	16.764			
3400	5.655	60.082	54.985	17.328			
3500	5.681	60.246	55.133	17.895			
3600	5.707	60.406	55.277	18.465			
3700	5.732	60.563	55.418	19.037			
3800	5.756	60.716	55.555	19.611			
3900	5.780	60.866	55.690	20.188			
4000	5.804	61.013	55.821	20.767			
4100	5.827	61.156	55.949	21.349			
4200	5.850	61.297	56.075	21.932			
4300	5.873	61.435	56.198	22.519			
4400	5.895	61.570	56.319	23.107			
4500	5.917	61.703	56.437	23.698			
4600	5.939	61.833	56.553	24.290			
4700	5.960	61.961	56.666	24.885			
4800	5.982	62.087	56.778	25.483			
4900	6.003	62.210	56.888	26.082			
5000	6.024	62.332	56.995	26.683			
5100	6.046	62.451	57.101	27.287			
5200	6.067	62.569	57.205	27.892			
5300	6.089	62.685	57.307	28.500			
5400	6.111	62.799	57.408	29.110			
5500	6.133	62.911	57.507	29.722			
5600	6.155	63.022	57.605	30.337			
5700	6.178	63.131	57.701	30.953			
5800	6.202	63.239	57.795	31.572			
5900	6.225	63.345	57.888	32.194			
6000	6.250	63.450	57.980	32.817			

PLATINUM IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	±.000	±.002	±.003	±.000			
1000	±.000	±.003	±.003	±.000			
2000	±.000	±.003	±.003	±.000			
3000	±.000	±.003	±.003	±.001			
4000	±.000	±.003	±.003	±.001			
5000	±.001	±.003	±.003	±.001			
6000	±.001	±.003	±.003	±.002			

15. Platinum

The ideal monatomic gas thermodynamic functions of platinum in Table XXXVI were calculated from the energy levels given by Moore[221] with the computer program discussed in section III-D. Uncertainty estimates are summarized on the back of the table.

16. Rhenium

The ideal monatomic gas thermodynamic functions of rhenium in Table XXXVII were computed from the energy levels listed by Moore[221] with the computer program discussed in section III-D. Uncertainty estimates are summarized on the back of the table.

TABLE XXXVII

IDEAL MONATOMIC GAS

gfw = 186.22

T, °K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal/gfw)	ΔH_f° (Kcal/gfw)	ΔF_f° (Kcal/gfw)	Log K_f
0	0.000	0.000	Infinite				Infinite
298.15	4.968	45.133	45.133	0.000			
300	4.968	45.163	45.133	0.009			
400	4.968	46.593	45.328	0.506			
500	4.968	47.701	45.696	1.003			
600	4.968	48.607	46.108	1.500			
700	4.968	49.373	46.521	1.996			
800	4.968	50.036	46.920	2.493			
900	4.968	50.622	47.299	2.990			
1000	4.968	51.145	47.658	3.487			
1100	4.968	51.619	47.997	3.984			
1200	4.969	52.051	48.317	4.481			
1300	4.971	52.449	48.620	4.978			
1400	4.974	52.817	48.907	5.475			
1500	4.979	53.160	49.179	5.972			
1600	4.989	53.482	49.438	6.471			
1700	5.004	53.785	49.685	6.970			
1800	5.025	54.071	49.921	7.472			
1900	5.056	54.344	50.146	7.976			
2000	5.097	54.604	50.363	8.483			
2100	5.150	54.854	50.571	8.995			
2200	5.218	55.095	50.771	9.514			
2300	5.301	55.329	50.964	10.040			
2400	5.401	55.557	51.151	10.574			
2500	5.518	55.779	51.331	11.120			
2600	5.655	55.998	51.507	11.679			
2700	5.810	56.215	51.677	12.252			
2800	5.984	56.429	51.843	12.841			
2900	6.178	56.642	52.005	13.449			
3000	6.390	56.855	52.163	14.078			
3100	6.620	57.069	52.318	14.728			
3200	6.866	57.283	52.469	15.402			
3300	7.127	57.498	52.619	16.101			
3400	7.402	57.715	52.765	16.828			
3500	7.688	57.933	52.910	17.582			
3600	7.984	58.154	53.052	18.366			
3700	8.288	58.377	53.193	19.179			
3800	8.596	58.602	53.333	20.023			
3900	8.908	58.829	53.471	20.899			
4000	9.220	59.059	53.608	21.805			
4100	9.531	59.290	53.743	22.743			
4200	9.838	59.524	53.878	23.711			
4300	10.138	59.759	54.012	24.710			
4400	10.431	59.995	54.145	25.739			
4500	10.714	60.233	54.278	26.796			
4600	10.986	60.471	54.410	27.881			
4700	11.244	60.710	54.542	28.993			
4800	11.489	60.950	54.673	30.129			
4900	11.719	61.189	54.803	31.290			
5000	11.932	61.428	54.933	32.473			
5100	12.130	61.666	55.063	33.676			
5200	12.311	61.903	55.192	34.898			
5300	12.475	62.139	55.321	36.138			
5400	12.623	62.374	55.450	37.393			
5500	12.754	62.607	55.578	38.662			
5600	12.869	62.838	55.705	39.943			
5700	12.968	63.066	55.832	41.235			
5800	13.052	63.293	55.959	42.536			
5900	13.122	63.516	56.085	43.845			
6000	13.178	63.738	56.211	45.160			

RHENIUM IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	cal/°K gfw			Kcal/gfw			
	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	±.000	±.002	±.002	±.000			
1000	±.000	±.002	±.003	±.000			
2000	±.000	±.002	±.003	±.000			
3000	±.001	±.003	±.003	± .001			
4000	±.003	±.003	±.003	±.002			
5000	±.006	±.004	±.003	±.006			
6000	±.009	±.005	±.003	±.013			

<u>TABLE XXXVIII</u>

[illegible] IDEAL MONATOMIC GAS Ph

gfw [illegible] .91

	cal/°K gfw			Kcal/gfw			
T °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
[illegible]	0.000	0.000	Infinite				[illegible]
298.15	5.023	44.388	44.388	0.000			
300	5.025	44.419	44.388	0.009			
400	5.174	45.883	44.587	0.518			
500	5.386	47.060	44.967	1.046			
600	5.618	48.062	45.402	1.596			
700	5.839	48.945	45.846	2.169			
800	6.034	49.738	46.284	2.763			
900	6.198	50.458	46.708	3.375			
1000	6.329	51.118	47.117	4.002			
1100	6.430	51.727	47.508	4.640			
1200	6.505	52.290	47.884	5.287			
1300	6.558	52.812	48.243	5.940			
1400	6.594	53.300	48.587	6.598			
1500	6.617	53.756	48.917	7.259			
1600	6.629	54.183	49.232	7.921			
1700	6.635	54.585	49.536	8.584			
1800	6.636	54.965	49.827	9.248			
1900	6.634	55.323	50.107	9.911			
2000	6.631	55.663	50.376	10.575			
2100	6.626	55.987	50.636	11.237			
2200	6.623	56.295	50.886	11.900			
2300	6.620	56.589	51.128	12.562			
2400	6.618	56.871	51.361	13.224			
2500	6.618	57.141	51.587	13.886			
2600	6.620	57.401	51.806	14.548			
2700	6.623	57.651	52.017	15.210			
2800	6.627	57.892	52.223	15.872			
2900	6.634	58.124	52.422	16.535			
3000	6.641	58.349	52.616	17.199			
3100	6.650	58.567	52.805	17.864			
3200	6.660	58.779	52.988	18.529			
3300	6.671	58.984	53.167	19.196			
3400	6.683	59.183	53.341	19.863			
3500	6.695	59.377	53.511	20.532			
3600	6.708	59.566	53.676	21.202			
3700	6.721	59.750	53.838	21.874			
3800	6.735	59.929	53.996	22.547			
3900	6.749	60.104	54.150	23.221			
4000	6.764	60.275	54.301	23.897			
4100	6.778	60.442	54.449	24.574			
4200	6.793	60.606	54.594	25.252			
4300	6.808	60.766	54.735	25.932			
4400	6.823	60.923	54.874	26.614			
4500	6.839	61.076	55.010	27.297			
4600	6.854	61.227	55.144	27.982			
4700	6.870	61.374	55.275	28.668			
4800	6.887	61.519	55.403	29.356			
4900	6.903	61.661	55.530	30.045			
5000	6.920	61.801	55.654	30.736			
5100	6.937	61.938	55.775	31.429			
5200	6.955	62.073	55.895	32.124			
5300	6.973	62.206	56.013	32.820			
5400	6.992	62.336	56.129	33.518			
5500	7.011	62.465	56.243	34.218			
5600	7.030	62.591	56.355	34.921			
5700	7.051	62.716	56.466	35.625			
5800	7.072	62.838	56.575	36.331			
5900	7.093	62.960	56.682	37.039			
6000	7.115	63.079	56.787	37.749			

RHODIUM IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal/gfw)	ΔH_f° (Kcal/gfw)	ΔF_f° (Kcal/gfw)	Log K_p
298.15	±.000	±.002	±.002	±.000			
1000	±.001	±.002	±.003	±.000			
2000	±.001	±.003	±.003	±.001			
3000	±.001	±.003	±.003	±.001			
4000	±.001	±.003	±.003	±.002			
5000	±.001	±.003	±.003	±.002			
6000	±.001	±.003	±.003	±.003			

17. Rhodium

The ideal monatomic gas thermodynamic functions of rhodium in Table XXXVIII were calculated from the energy levels listed by Moore[221] with the computer program discussed in section III-D. Uncertainty estimates are summarized on the back of the table.

18. Scandium

a. Crystal Structure, Transition Point and Melting Point

At room temperature, elemental scandium has a hexagonal, close-packed structure.[311,312,315,316] A face-centered cubic form reported by Meisel[313] has been attributed[311,314] to ScN. Spedding and Daane[315] reported an allotropic transition at 1608 °K. Mardon et al[316] found a thermal arrest corresponding to a transition at 1646 °± 10 °K. The last authors stated that the transition was expected to be to a body-centered cubic structure by analogy with certain of the rare earth elements.

Spedding et al[311,315] found the melting point of scandium to be 1812 ° ± 2 °K. Mardon et al[316] reported a melting point of 1795 ° ± 5 °K for metal which had picked up an "appreciable" but unspecified amount of tantalum. The transition and melting points adopted herein were those reported by Spedding et al.[311,315] Uncertainties of ±15 ° and ± 5 °K, respectively, were assigned. Other compilers [56,77] had recently assumed the melting point to be 1673 °K.

b. Thermodynamic Properties

1) Heat of transition

The heat of transition of scandium at 1608 °K was estimated to be 350 ± 100 cal/gfw.

2) Heat of fusion

The heat of fusion of scandium had not been measured. It was estimated herein to be 3770 ± 200 cal/gfw on the assumption that

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[311] Spedding, F. H., A. H. Daane, G. F. Wakefield, and D. H. Dennison, Trans. Met. Soc. AIME 218, 608 (1960).

[312] Spedding, F. H., K. W. Herrman, and A. H. Daane, Acta Cryst. 9, 559 (1956).

[313] Meisel, K., Naturwiss. 27, 230 (1939).

[314] Klemm, W., Anorganische Chemie 1, 48 (1948).

[315] Spedding, F. H. and A. H. Daane, Met. Revs. 5, 297 (1960).

[316] Mardon, P. G., J. L. Nichols, J. H. Pearce and D. M. Poole, Nature 189, 566 (1961).

TABLE XXXIX

SCANDIUM — REFERENCE STATE — Sc

Reference State for Calculating ΔH_f°, ΔF_f°, and $\text{Log } K_p$: Solid from 298.15° to 1812°K, Liquid from 1812° to 3021°K, Gas from 3021° to 6000°K.

gfw = 44.96 — T_t = 1608° ± 15°K — m.p. = 1812° ± 5°K — b.p. = 3021° ± 140°K

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-1.280			
298.15	6.000	9.000	9.000	0.000			
300	6.002	9.037	9.000	0.011			
400	6.110	10.778	9.236	0.617			
500	6.218	12.154	9.688	1.233			
600	6.326	13.297	10.197	1.860			
700	6.434	14.280	10.711	2.498			
800	6.542	15.146	11.212	3.147			
900	6.650	15.923	11.693	3.807			
1000	6.758	16.629	12.152	4.477			
1100	6.866	17.278	12.589	5.158			
1200	6.974	17.880	13.005	5.850			
1300	7.082	18.443	13.402	6.553			
1400	7.190	18.972	13.782	7.267			
1500	7.328	19.471	14.144	7.991			
1600	7.406	19.946	14.492	8.726			
1608	7.415	19.984	14.520	8.786			
1608	8.000	20.202	14.520	9.136			
1700	8.000	20.647	14.840	9.872			
1800	8.000	21.104	15.175	10.672			
1812	8.000	21.158	15.215	10.768			
1812	8.000	23.238	15.215	14.538			
1900	8.000	23.618	15.596	15.242			
2000	8.000	24.028	16.007	16.042			
2100	8.000	24.418	16.398	16.842			
2200	8.000	24.790	16.771	17.642			
2300	8.000	25.146	17.128	18.442			
2400	8.000	25.486	17.468	19.242			
2500	8.000	25.813	17.796	20.042			
2600	8.000	26.127	18.111	20.842			
2700	8.000	26.429	18.413	21.642			
2800	8.000	26.720	18.705	22.442			
2900	8.000	27.000	18.986	23.242			
3000	8.000	27.271	19.257	24.042			
3021	8.000	27.326	19.312	24.210			
3021	6.248	53.651	19.312	103.731			
3100	6.397	53.815	20.193	104.229			
3200	6.599	54.021	21.246	104.879			
3300	6.810	54.227	22.242	105.549			
3400	7.031	54.434	23.187	106.241			
3500	7.259	43.641	24.082	106.955			
3600	7.492	54.849	24.934	107.693			
3700	7.730	55.057	25.745	108.454			
3800	7.969	55.267	26.520	109.239			
3900	8.208	55.477	27.260	110.048			
4000	8.446	55.688	27.968	110.881			
4100	8.680	55.899	28.646	111.737			
4200	8.909	56.111	29.298	112.616			
4300	9.132	56.323	29.923	113.518			
4400	9.347	56.536	30.526	114.442			
4500	9.554	56.748	31.106	115.388			
4600	9.750	56.960	31.666	116.353			
4700	9.936	57.172	32.207	117.337			
4800	10.111	57.383	32.729	118.340			
4900	10.274	57.593	33.234	119.359			
5000	10.425	57.802	33.723	120.394			
5100	10.563	58.010	34.197	121.444			
5200	10.689	58.216	34.657	122.506			
5300	10.803	58.421	35.104	123.581			
5400	10.905	58.624	35.538	124.667			
5500	10.994	58.825	35.959	125.762			
5600	11.072	59.024	36.370	126.865			
5700	11.139	59.220	36.768	127.976			
5800	11.196	59.415	37.158	129.093			
5900	11.242	59.606	37.536	130.215			
6000	11.279	59.796	37.906	131.341			

SCANDIUM REFERENCE STATE

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal/gfw)	ΔH_f° (Kcal/gfw)	ΔF_f° (Kcal/gfw)	Log K_p
0				± .040			
298.15	± .200	± .500	± .500	± .000			
1000	± .350	± .830	± .640	± .190			
1608	± .500	±1.090	± .800	± .460			
1608	±1.000	±1.150	± .800	± .560			
1812	±1.500	±1.300	± .850	± .810			
1812	± .400	±1.410	± .850	±1.010			
3021	±2.300	±2.100	±1.220	±2.640			
3021	± .001	± .002					
4000	± .002	± .003					
5000	± .002	± .003					
6000	± .002	± .003					

TABLE XL

SCANDIUM — IDEAL MONATOMIC GAS — Sc

Reference State for Calculating ΔH_f°, ΔF_f°, and Log K_p : Solid from 298.15° to 1812°K, Liquid from 1812° to 3021°K, Gas from 3021° to 6000°K.

gfw = 44.96 — T_t = 1608°± 15°K — m.p. = 1812° ± 5°K — b.p. = 3021° ± 140°K

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-1.674	89.106	89.106	Infinite
298.15	5.283	41.750	41.750	0.000	89.500	79.736	-58.445
300	5.279	41.783	41.750	0.010	89.499	79.665	-58.033
400	5.148	43.281	41.955	0.530	89.413	76.412	-41.748
500	5.085	44.422	42.339	1.042	89.309	73.174	-31.983
600	5.049	45.346	42.765	1.548	89.188	69.959	-25.480
700	5.028	46.122	43.191	2.052	89.054	66.763	-20.843
800	5.014	46.793	43.600	2.554	88.907	63.590	-17.371
900	5.004	47.383	43.988	3.055	88.748	60.434	-14.675
1000	4.997	47.909	44.355	3.555	88.578	57.297	-12.522
1100	4.992	48.386	44.700	4.054	88.396	54.178	-10.764
1200	4.989	48.820	45.025	4.553	88.203	51.076	-9.302
1300	4.988	49.219	45.333	5.052	87.999	47.990	-8.067
1400	4.989	49.589	45.624	5.551	87.784	44.921	-7.012
1500	4.993	49.933	45.900	6.050	87.559	41.866	-6.100
1600	5.001	50.256	46.162	6.550	87.324	38.828	-5.303
1608	5.002	50.280	46.182	6.590	87.304	38.587	-5.244
1608	5.002	50.280	46.182	6.590	86.954	38.587	-5.244
1700	5.014	50.559	46.412	7.050	86.678	35.828	-4.606
1800	5.034	50.846	46.650	7.553	86.381	32.845	-3.988
1812	5.037	50.879	46.677	7.614	86.346	32.490	-3.919
1812	5.037	50.879	46.677	7.614	82.576	32.490	-3.919
1900	5.062	51.119	46.878	8.058	82.316	30.064	-3.458
2000	5.099	51.380	47.097	8.566	82.024	27.320	-2.985
2100	5.148	51.630	47.307	9.078	81.736	24.591	-2.559
2200	5.208	51.870	47.509	9.595	81.453	21.876	-2.173
2300	5.282	52.103	47.704	10.120	81.178	19.175	-1.822
2400	5.369	52.330	47.892	10.652	80.910	16.482	-1.501
2500	5.472	52.551	48.074	11.194	80.652	13.805	-1.207
2600	5.589	52.768	48.250	11.747	80.405	11.139	-0.936
2700	5.722	52.981	48.421	12.312	80.170	8.478	-0.686
2800	5.869	53.192	48.588	12.892	79.950	5.828	-0.455
2900	6.032	53.401	48.750	13.487	79.745	3.184	-0.240
3000	6.208	53.608	48.909	14.099	79.557	0.544	-0.040
3021	6.248	53.651	48.941	14.231	79.521	0.000	0.000
3021	6.248	53.651	48.941	14.231			
3100	6.397	53.815	49.064	14.729			
3200	6.599	54.021	49.215	15.379			
3300	6.810	54.227	49.364	16.049			
3400	7.031	54.434	49.510	16.741			
3500	7.259	54.641	49.654	17.455			
3600	7.492	54.849	49.795	18.193			
3700	7.730	55.057	49.935	18.954			
3800	7.969	55.267	50.072	19.739			
3900	8.208	55.477	50.208	20.548			
4000	8.446	55.688	50.342	21.381			
4100	8.680	55.899	50.475	22.237			
4200	8.909	56.111	50.607	23.116			
4300	9.132	56.323	50.738	24.018			
4400	9.347	56.536	50.867	24.942			
4500	9.554	56.748	50.995	25.888			
4600	9.750	56.960	51.123	26.853			
4700	9.936	57.172	51.249	27.837			
4800	10.111	57.383	51.375	28.840			
4900	10.274	57.593	51.499	29.859			
5000	10.425	57.802	51.623	30.894			
5100	10.563	58.010	51.747	31.944			
5200	10.689	58.216	51.869	33.006			
5300	10.803	58.421	51.991	34.081			
5400	10.905	58.624	52.112	35.167			
5500	10.994	58.825	52.232	36.262			
5600	11.072	59.024	52.351	37.365			
5700	11.139	59.220	52.470	38.476			
5800	11.196	59.415	52.588	39.593			
5900	11.242	59.606	52.706	40.715			
6000	11.279	59.796	52.822	41.841			

SCANDIUM IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	±.000	±.002	±.002	±.000	± .500	± .650	±.480
1000	±.000	±.002	±.002	±.000	± .500	±1.060	±.230
1608	±.000	±.002	±.002	±.000	± .500	±1.790	±.240
1608	±.000	±.002	±.002	±.000	± .600	±1.790	±.240
1812	±.000	±.002	±.003	±.000	± .850	±1.940	±.230
1812	±.000	±.002	±.003	±.000	±1.050	±1.940	±.230
3021	±.001	±.002	±.003	±.001	±2.680	±3.690	±.270
3021	±.001	±.002	±.003	±.001			
4000	±.002	±.003	±.003	±.002			
5000	±.002	±.003	±.003	±.004			
6000	±.002	±.003	±.003	±.005			

the entropy of transition plus the entropy of fusion was 2.3 cal/ °K gfw. The same entropy of transformation was adopted by Stull and Sinke[77] and Kelley.[56]

3) Entropy and heat content at 298.15 °K

No data were available for the low temperature heat capacity of scandium. The estimate of Brewer[317] of 9.0 cal/ °K gfw was adopted. This was also listed by Kelley and King[318] who assigned an uncertainty of 0.5 cal/ °K gfw. $H^\circ_{298} - H^\circ_0$ was estimated to be 1280 ± 40 cal/gfw for the solid.

4) High-temperature heat content

In the absence of experimental data, Kelley's[56] estimated heat capacity (in cal/ °K gfw) equation was used for the hexagonal-close-packed phase between 298.15° and 1608 °K.

$$C^\circ_p = 5.68 + 1.08 \times 10^{-3}T \quad . \tag{155}$$

For the high-temperature phase (presumably body-centered cubic), a constant heat capacity of 8.00 cal/ ° K gfw was assumed. Kelley's[56] estimate of 8.00 cal/° K gfw was used for the heat capacity of liquid scandium.

5) Heat of sublimation, heat of vaporization, and boiling point

The vapor pressure of scandium was reported by Spedding et al.[311] From their data and the free-energy functions tabulated here, the heat of sublimation at 298.15 °K was calculated to be 89.50 ± 0.50 Kcal/gfw. The normal boiling point of scandium was calculated to be 3021° ± 140 °K, and the heat of vaporization at the normal boiling point was found to be 79.521 ± 2.7 Kcal/gfw. Stull and Sinke[77] had previously estimated the heat of sublimation at 298.15 °K to be 82.0 Kcal/gfw, the heat of vaporization to be 72.850 Kcal/gfw, and the normal boiling point to be 2750 °K.

6) Thermodynamic functions

The reference state thermodynamic functions of scandium are given in Table XXXIX. The ideal monatomic gas thermodynamic functions of scandium given in Table XL were calculated from all the energy levels listed by Moore[52] with the computer program discussed in section III-D. Uncertainty estimates are summarized on the back of the tables. $H^\circ_{298} - H^\circ_0$ was found to be 1,674 cal/mole for the ideal gas.

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[317] Brewer, L., Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics, Natl. Nuclear Energy Ser. IV-19B (L. L. Quill, ed.), McGraw-Hill, N.Y. (1950), chap. 3.

[318] Kelley, K. K. and E. G. King, Contributions to the Data on Theroetical Metallurgy, XIV. Entropies of Inorganic Substances, Bur. Mines Bull.592 (to be published).

19. Silicon

The ideal monatomic gas thermodynamic functions of silicon given in Table XLI were calculated from the energy levels listed by Moore[52] with the computer program discussed in section III-D. Uncertainty estimates are summarized on the back of the table.

gfw = 28.09

T, °K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal/gfw)	ΔH_f° (Kcal/gfw)	ΔF_f° (Kcal/gfw)	Log K_p
0	0.000	0.000	Infinite				Infinite
298.15	5.319	40.123	40.123	0.000			
300	5.315	40.156	40.123	0.010			
400	5.166	41.662	40.330	0.533			
500	5.095	42.806	40.715	1.046			
600	5.056	43.731	41.143	1.553			
700	5.033	44.509	41.570	2.057			
800	5.019	45.180	41.980	2.560			
900	5.012	45.770	42.369	3.061			
1000	5.012	46.299	42.736	3.563			
1100	5.017	46.776	43.082	4.064			
1200	5.027	47.213	43.408	4.566			
1300	5.043	47.616	43.717	5.070			
1400	5.063	47.991	44.009	5.575			
1500	5.087	48.341	44.286	6.082			
1600	5.113	48.670	44.550	6.592			
1700	5.142	48.981	44.801	7.105			
1800	5.172	49.276	45.042	7.621			
1900	5.202	49.556	45.272	8.139			
2000	5.232	49.824	45.493	8.661			
2100	5.261	50.080	45.705	9.186			
2200	5.289	50.325	45.910	9.713			
2300	5.316	50.561	46.107	10.243			
2400	5.341	50.787	46.297	10.776			
2500	5.365	51.006	46.481	11.312			
2600	5.386	51.217	46.659	11.849			
2700	5.406	51.420	46.832	12.389			
2800	5.424	51.617	46.999	12.930			
2900	5.440	51.808	47.162	13.473			
3000	5.454	51.993	47.320	14.018			
3100	5.467	52.172	47.473	14.564			
3200	5.478	52.345	47.623	15.111			
3300	5.487	52.514	47.769	15.660			
3400	5.495	52.678	47.911	16.209			
3500	5.502	52.837	48.049	16.759			
3600	5.508	52.992	48.184	17.309			
3700	5.513	53.143	48.316	17.860			
3800	5.516	53.291	48.445	18.412			
3900	5.519	53.434	48.571	18.964			
4000	5.521	53.574	48.695	19.515			
4100	5.522	53.710	48.815	20.068			
4200	5.522	53.843	48.934	20.620			
4300	5.522	53.973	49.049	21.172			
4400	5.522	54.100	49.163	21.724			
4500	5.521	54.224	49.274	22.276			
4600	5.520	54.345	49.383	22.829			
4700	5.518	54.464	49.489	23.380			
4800	5.517	54.580	49.594	23.932			
4900	5.515	54.694	49.697	24.484			
5000	5.513	54.805	49.798	25.035			
5100	5.512	54.915	49.898	25.587			
5200	5.510	55.022	49.995	26.138			
5300	5.509	55.126	50.091	26.689			
5400	5.508	55.229	50.185	27.239			
5500	5.508	55.330	50.278	27.790			
5600	5.507	55.430	50.369	28.341			
5700	5.508	55.527	50.458	28.892			
5800	5.509	55.623	50.547	29.443			
5900	5.511	55.717	50.634	29.994			
6000	5.514	55.810	50.719	30.545			

SILICON IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	cal/°K gfw			Kcal/gfw			
	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	±.000	±.002	±.002	±.000			
1000	±.000	±.002	±.002	±.000			
2000	±.000	±.002	±.002	±.000			
3000	±.000	±.002	±.003	±.001			
4000	±.000	±.002	±.003	±.001			
5000	±.000	±.002	±.003	±.001			
6000	±.001	±.003	±.003	±.002			

20. Strontium

a. Crystal Structure, Transition Point, and Melting Point

Three allotropic modifications of elemental strontium have been reported.[319-321, 129, 322] They are α-Sr with a face-centered cubic structure, β-Sr with a hexagonal, close-packed structure, and γ-Sr with a body-centered structure. The transitions are summarized by equation (156):

$$\alpha - \mathrm{Sr} \overset{T_1}{\rightleftharpoons} \beta - \mathrm{Sr} \overset{T_2}{\rightleftharpoons} \gamma - \mathrm{Sr} \tag{156}$$

Rinck,[319] using thermal analysis, dilatometric studies, and electrical measurements, gave T_1 as 508°K and T_2 as 813°K. Sheldon and King,[320] using high-temperature X-ray techniques, found T_1 and T_2 to be $488° \pm 10°$ and $878° \pm 10°K$, respectively. Hirst, King, and Kanda[321] reported $486° \pm 10°$ and $881° \pm 10°K$ to be the two transition temperatures, and Schottmiller, King, and Kanda[129] give the temperatures as $503° \pm 6°$ and $894° \pm 6°K$.

In view of Smith, Carlson, and Vest's[124] demonstration that two of the four reported allotropic modifications of calcium were caused by impurities, it would not be surprising to find a similar situation with strontium. Kelley[56] and Stull and Sinke[77] used a single transition at 862°K in their compilations. However, the evidence for this transition temperature is not at all conclusive. It has been reported by Eastman, Cubicciotti, and Thurmond,[323] and was tabulated by Kubaschewski et al[79] in their review. The latter authors did not specify the source of the data, and Kubaschewski and Evans[182] later listed the data of Rinck[319] in their book. A single transition at 862°K (face-centered cubic to body-centered cubic) has been adopted here and assigned an uncertainty of ±50°K.

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[319] Rinck, E., Compt. rend. 234, 845 (1952).

[320] Sheldon, E. A. and A. J. King, Acta Cryst. 6, 100 (1953).

[321] Hirst, R. J., A. J. King, and F. A. Kanda, J. Phys. Chem. 60, 302 (1956).

[322] Klemm, W. and G. Mika, Z. anorg. Chem. 248, 155 (1941).

[323] Eastman, E. D., D. D. Cubicciotti, and C. D. Thurmond, Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics, Natl. Nuclear Energy Ser. IV-19B (L. L. Quill, ed.), McGraw-Hill, N. Y. (1950), chap. 5.

The melting point of strontium was taken to be $1045^{\circ} \pm 4^{\circ}K$. The more reliable values in the literature[132, 129, 321] ranged from 1041° to $1047^{\circ}K$. Stull and Sinke[77] and Kelley[56] used $1043^{\circ}K$.

b. Thermodynamic Properties

1) Heat of transition

The heat (or heats) of transition of strontium has not been measured. Stull and Sinke's[77] estimate of 200 cal/gfw for the single, assumed transition was adopted here. This estimate, arrived at by analogy with calcium, was assigned an uncertainty of 100 cal/gfw.

2) Heat of fusion

There were no measurements reported for the heat of fusion of strontium. Kubaschewski et al[79] estimated the sum of the entropies of fusion and transition to be 2.12 cal/$^{\circ}$K gfw from regularities among the alkali and alkaline earth metals. The heat of fusion was then calculated to be 1970 cal/gfw and was assigned an uncertainty of ± 150 cal/gfw. Stull and Sinke[77] and Kelley[56] used 2200 cal/gfw for the heat of fusion of strontium from the same total entropy of transformation, but without subtracting the entropy of transition. Kubaschewski's values were were used herein.

3) Entropy and heat content at 298.15°K

The low-temperature heat capacity of strontium had not been measured. Kelley and King[318] estimated the entropy at $298.15^{\circ}K$ to be 12.5 ± 0.5 cal/$^{\circ}$K gfw; this estimate was accepted here. Latimer[324] and NBS Circular 500 reviewer estimated a value of 13.0 cal/$^{\circ}$K gfw for this quantity. $H^{o}_{298} - H^{o}_{0}$ for strontium was estimated to be 1550 ± 150 cal/gfw from a plot of $H^{o}_{298} - H^{o}_{0}$ versus S^{o}_{298} for the alkali and alkaline earth metals and the estimated value of S^{o}_{298} for strontium.

4) High temperature heat content

No experimental data were available for the high-temperature heat capacity or heat content of strontium. Stull and Sinke[77] and Kelley[56] in their compilations assumed that these quantities for α-Sr were essentially identical to those for α-Ca, and extrapolated the α-Ca data to the transition point of strontium.

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[324] Latimer, W. M., Oxidation Potentials, 2nd ed., Prentice-Hall, N. Y. (1952).

Stull and Sinke[77] extended this procedure for γ-Sr. Kelley[56] assumed a constant heat capacity of 9.16 cal/°K gfw for γ-Sr. The latter was an average of heat capacities obtained by the application of an equation for the heat capacity of γ-Ca to γ-Sr.

The present compilation for α-Sr is based on assumed heat capacities (in cal/°K gfw) over the range from 298.15° to 862°K given by equation (157).

$$C_p = 5.207 + 4.00 \times 10^{-3} T \quad . \tag{157}$$

This equation yields the adopted heat capacity of 6.400 cal/°K gfw at 298.15°K (compared with a heat capacity of 6.280 cal/°K gfw for α-Ca at the same temperature) and a temperature coefficient of the heat capacity about 10 percent greater than that for α-Ca. The assigned uncertainties for the heat capacity of α-Sr were about double the value of those used previously for α-Ca.

Kelley's[56] estimate of 9.16 cal/°K gfw was adopted for the heat capacity of γ-Sr with increased uncertainties over those used for γ-Ca.

Stull and Sinke[77] and Kelley[56] assumed a constant heat capacity of 7.4 cal/°K gfw for liquid strontium. The somewhat larger value of 7.8 cal/°K gfw was used here with an assigned uncertainty which increases with temperature.

5) Heat of formation of the monatomic gas

The free-energy functions tabulated here were used with vapor pressure data from the following sources to calculate the indicated heats of formation at 298.15°K using the Third Law Method:

Source	Temperature Range (°K)	$\Delta H^{o}_{f\,298}$ (Kcal/gfw)
Hartmann and Schneider[148]	1199-1379	39.490 $\pm$ 0.110
Priselkov and Nesmeyanov[147]	673- 873	38.640 $\pm$ 0.400
Ruff and Hartmann[153]	1217-1411	38.000 $\pm$ 2.500

Unsmoothed vapor pressure data were used for these calculations.

An average of the first two values, 39.070 $\pm$ 0.500 Kcal/gfw, was adopted for the heat of sublimation of strontium at 298.15°K.

The boiling point of strontium was calculated to be 1641° $\pm$ 90°K, and the heat of vaporization at the boiling point was found to be 33.012 $\pm$ 1.05 Kcal/gfw.

6) Thermodynamic functions

The reference state thermodynamic functions of strontium obtained here are given in Table XLII. The ideal monatomic gas thermodynamic functions of stronium given in Table XLIII were calculated from all the energy levels listed by Moore[253] with the computer program described in section III-D. Uncertainty estimates are summarized on the back of the tables. $H^\circ_{298} - H^\circ_0$ was found to be 1,481 cal/mole for the ideal gas.

TABLE XLII

STRONTIUM — REFERENCE STATE — Sr

Reference State for Calculating ΔH_f°, ΔF_f°, and $\text{Log } K_p$: Solid from 298.15° to 1045°K, Liquid from 1045° to 1641°K, Gas from 1641° to 6000°K.

gfw = 87.63 — T_t = 862°K ± 50°K — m.p. = 1045° ± 4°K — b.p. = 1641° ± 90°K

T,°K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal/gfw)	ΔH_f° (Kcal/gfw)	ΔF_f° (Kcal/gfw)	Log K_p
0	0.000	0.000	Infinite	-1.550			
298.15	6.400	12.500	12.500	0.000			
300	6.407	12.540	12.501	0.012			
400	6.807	14.438	12.757	0.673			
500	7.207	15.999	13.253	1.373			
600	7.607	17.349	13.826	2.114			
700	8.007	18.551	14.416	2.895			
800	8.407	19.647	15.003	3.715			
862	8.655	20.283	15.359	4.244			
862	9.160	20.515	15.359	4.444			
900	9.160	20.910	15.586	4.792			
1000	9.160	21.875	16.167	5.708			
1045	9.160	22.278	16.421	6.120			
1045	7.800	24.163	16.421	8.090			
1100	7.800	24.563	16.818	8.519			
1200	7.800	25.242	17.493	9.299			
1300	7.800	25.866	18.113	10.079			
1400	7.800	26.444	18.688	10.859			
1500	7.800	26.982	19.223	11.639			
1600	7.800	27.486	19.724	12.419			
1641	7.800	27.680	19.922	12.731			
1641	4.977	47.797	19.922	45.743			
1700	4.981	47.975	20.895	46.036			
1800	4.991	48.260	22.407	46.525			
1900	5.007	48.530	23.775	47.035			
2000	5.031	48.787	25.019	47.537			
2100	5.065	49.033	26.156	48.041			
2200	5.111	49.270	27.202	48.550			
2300	5.171	49.499	28.167	49.064			
2400	5.249	49.720	29.060	49.585			
2500	5.345	49.936	29.890	50.114			
2600	5.461	50.148	30.666	50.654			
2700	5.600	50.357	31.391	51.207			
2800	5.762	50.563	32.072	51.775			
2900	5.949	50.769	32.713	52.361			
3000	6.159	50.974	33.319	52.966			
3100	6.394	51.180	33.892	53.593			
3200	6.653	51.387	34.435	54.245			
3300	6.933	51.596	34.952	54.924			
3400	7.235	51.807	35.444	55.633			
3500	7.556	52.021	35.915	56.372			
3600	7.894	52.239	36.365	57.144			
3700	8.247	52.460	36.797	57.951			
3800	8.611	52.685	37.213	58.794			
3900	8.984	52.913	37.612	59.674			
4000	9.364	53.145	37.997	60.591			
4100	9.747	53.381	38.370	61.547			
4200	10.131	53.621	38.730	62.541			
4300	10.513	53.864	39.080	63.573			
4400	10.891	54.110	39.418	64.643			
4500	11.262	54.359	39.748	65.751			
4600	11.625	54.610	40.068	66.895			
4700	11.979	54.864	40.380	68.076			
4800	12.320	55.120	40.684	69.291			
4900	12.650	55.377	40.981	70.539			
5000	12.965	55.636	41.272	71.820			
5100	13.267	55.896	41.556	73.132			
5200	13.554	56.156	41.833	74.473			
5300	13.826	56.417	42.107	75.842			
5400	14.082	56.678	42.374	77.238			
5500	14.324	56.938	42.636	78.658			
5600	14.550	57.198	42.894	80.102			
5700	14.762	57.458	43.148	81.568			
5800	14.959	57.716	43.396	83.054			
5900	15.141	57.974	43.642	84.559			
6000	15.309	58.230	43.883	86.081			

STRONTIUM REFERENCE STATE

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal/°K gfw			Kcal/gfw			
0				±.150			
298.15	± .200	± .500	±.500	±.000			
862	± .300	± .610	±.540	±.060			
862	± .600	± .730	±.540	±.160			
1045	±1.000	± .760	±.580	±.190			
1045	± .500	± .910	±.580	±.340			
1641	±1.500	±1.130	±.740	±.640			
1641	± .000	± .002					
2000	± .000	± .002					
3000	± .001	± .002					
4000	± .002	± .003					
5000	± .003	± .003					
6000	± .003	± .003					

TABLE XLIII

STRONTIUM — IDEAL MONATOMIC GAS — Sr

Reference State for Calculating ΔH_f°, ΔF_f°, and $\text{Log } K_p$: Solid from 298.15° to 1045°K, Liquid from 1045° to 1641°K, Gas from 1641° to 6000°K.

gfw = 87.63 — T_t = 862° ± 50°K — m.p. = 1045° ± 4°K — b.p. = 1641° ± 90°K

	cal/°K gfw			Kcal/gfw				
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-1.481	39.139	39.139	Infinite
298.15	4.968	39.325	39.325	0.000	39.070	31.072	-22.775
300	4.968	39.356	39.325	0.009	39.067	31.023	-22.599
400	4.968	40.785	39.520	0.506	38.903	28.365	-15.497
500	4.968	41.894	39.888	1.003	38.700	25.752	-11.256
600	4.968	42.799	40.300	1.500	38.456	23.186	-8.445
700	4.968	43.565	40.713	1.996	38.171	20.662	-6.451
800	4.968	44.229	41.112	2.493	37.848	18.183	-4.967
862	4.968	44.600	41.350	2.801	37.627	16.666	-4.225
862	4.968	44.600	41.350	2.801	37.427	16.666	-4.225
900	4.968	44.814	41.492	2.990	37.268	15.755	-3.826
1000	4.968	45.337	41.850	3.487	36.849	13.387	-2.926
1045	4.968	45.556	42.005	3.711	36.661	12.335	-2.580
1045	4.968	45.556	42.005	3.711	34.691	12.335	-2.580
1100	4.968	45.811	42.189	3.984	34.535	11.162	-2.218
1200	4.968	46.243	42.509	4.481	34.252	9.051	-1.648
1300	4.969	46.641	42.812	4.977	33.968	6.961	-1.170
1400	4.969	47.009	43.099	5.474	33.685	4.895	-0.764
1500	4.971	47.352	43.371	5.971	33.402	2.848	-0.415
1600	4.975	47.673	43.630	6.469	33.120	0.820	-0.112
1641	4.977	47.797	43.731	6.673	33.012	0.000	0.000
1641	4.977	47.797	43.731	6.673			
1700	4.981	47.975	43.877	6.966			
1800	4.991	48.260	44.112	7.465			
1900	5.007	48.530	44.338	7.965			
2000	5.031	48.787	44.554	8.467			
2100	5.065	49.033	44.761	8.971			
2200	5.111	49.270	44.961	9.480			
2300	5.171	49.499	45.153	9.994			
2400	5.249	49.720	45.339	10.515			
2500	5.345	49.936	45.519	11.044			
2600	5.461	50.148	45.693	11.584			
2700	5.600	50.357	45.862	12.137			
2800	5.762	50.563	46.026	12.705			
2900	5.949	50.769	46.186	13.291			
3000	6.159	50.974	46.342	13.896			
3100	6.394	51.180	46.495	14.523			
3200	6.653	51.387	46.644	15.175			
3300	6.933	51.596	46.791	15.854			
3400	7.235	51.807	46.936	16.563			
3500	7.556	52.021	47.078	17.302			
3600	7.894	52.239	47.218	18.074			
3700	8.247	52.460	47.357	18.881			
3800	8.611	52.685	47.494	19.724			
3900	8.984	52.913	47.630	20.604			
4000	9.364	53.145	47.765	21.521			
4100	9.747	53.381	47.899	22.477			
4200	10.131	53.621	48.033	23.471			
4300	10.513	53.864	48.165	24.503			
4400	10.891	54.110	48.298	25.573			
4500	11.262	54.359	48.430	26.681			
4600	11.625	54.610	48.561	27.825			
4700	11.979	54.864	48.693	29.006			
4800	12.320	55.120	48.824	30.221			
4900	12.650	55.377	48.955	31.469			
5000	12.965	55.636	49.086	32.750			
5100	13.267	55.896	49.217	34.062			
5200	13.554	56.156	49.348	35.403			
5300	13.826	56.417	49.479	36.772			
5400	14.082	56.678	49.610	38.168			
5500	14.324	56.938	49.741	39.588			
5600	14.550	57.198	49.871	41.032			
5700	14.762	57.458	50.002	42.498			
5800	14.959	57.716	50.133	43.984			
5900	15.141	57.974	50.264	45.489			
6000	15.309	58.230	50.394	47.011			

STRONTIUM IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	cal/°K gfw C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	Kcal/gfw $H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	±.000	±.002	±.002	±.000	± .500	± .560	±.410
862	±.000	±.002	±.002	±.000	± .500	±1.000	±.250
862	±.000	±.002	±.002	±.000	± .500	±1.000	±.250
1045	±.000	±.002	±.002	±.000	± .600	±1.200	±.250
1045	±.000	±.002	±.002	±.000	± .750	±1.200	±.250
1641	±.000	±.002	±.002	±.000	±1.050	±1.800	±.240
1641	±.000	±.002	±.002	±.000			
2000	±.000	±.002	±.002	±.000			
3000	±.001	±.002	±.002	±.001			
4000	±.002	±.003	±.003	±.002			
5000	±.003	±.003	±.003	±.004			
6000	±.003	±.003	±.003	±.006			

TANTALUM

TABLE XLIV
IDEAL MONATOMIC GAS

Ta

gfw = 180.95

T, °K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal/gfw)	ΔH_f° (Kcal/gfw)	ΔF_f° (Kcal/gfw)	Log K_p
0	0.000	0.000	Infinite				Infinite
298.15	4.985	44.243	44.243	0.000			
300	4.986	44.274	44.243	0.009			
400	5.081	45.719	44.440	0.512			
500	5.278	46.872	44.815	1.029			
600	5.541	47.857	45.241	1.570			
700	5.827	48.733	45.679	2.138			
800	6.110	49.530	46.111	2.735			
900	6.376	50.265	46.532	3.359			
1000	6.621	50.949	46.940	4.009			
1100	6.844	51.591	47.334	4.683			
1200	7.044	52.195	47.714	5.377			
1300	7.221	52.766	48.081	6.091			
1400	7.377	53.307	48.435	6.821			
1500	7.514	53.821	48.777	7.565			
1600	7.633	54.310	49.108	8.323			
1700	7.739	54.776	49.428	9.092			
1800	7.832	55.221	49.737	9.870			
1900	7.916	55.647	50.037	10.658			
2000	7.993	56.055	50.328	11.453			
2100	8.064	56.446	50.610	12.256			
2200	8.132	56.823	50.884	13.066			
2300	8.196	57.186	51.150	13.882			
2400	8.258	57.536	51.409	14.705			
2500	8.319	57.874	51.661	15.534			
2600	8.378	58.202	51.906	16.369			
2700	8.437	58.519	52.145	17.210			
2800	8.495	48.827	52.378	18.056			
2900	8.552	49.126	52.606	18.909			
3000	8.610	59.417	52.828	19.767			
3100	8.667	59.700	53.045	20.631			
3200	8.725	59.976	53.258	21.500			
3300	8.783	60.246	53.465	22.376			
3400	8.841	60.509	53.669	23.257			
3500	8.900	60.766	53.868	24.144			
3600	8.959	61.018	54.063	25.037			
3700	9.019	61.264	54.254	25.936			
3800	9.079	61.505	54.442	26.841			
3900	9.139	61.742	54.626	27.752			
4000	9.200	61.974	54.807	28.668			
4100	9.261	62.202	54.984	29.592			
4200	9.322	62.426	55.159	30.521			
4300	9.383	62.646	55.330	31.456			
4400	9.444	62.862	55.499	32.397			
4500	9.504	63.075	55.665	33.345			
4600	9.564	63.285	55.829	34.298			
4700	9.623	63.491	55.989	35.258			
4800	9.680	63.694	56.148	36.223			
4900	9.737	63.894	56.304	37.194			
5000	9.792	64.092	56.458	38.170			
5100	9.846	64.286	56.609	39.152			
5200	9.897	64.478	56.759	40.139			
5300	9.947	64.667	56.906	41.131			
5400	9.995	64.853	57.052	42.128			
5500	10.040	65.037	57.195	43.130			
5600	10.083	65.218	57.337	44.136			
5700	10.124	65.397	57.477	45.147			
5800	10.161	65.573	57.615	46.161			
5900	10.197	65.747	57.751	47.179			
6000	10.229	65.919	57.886	48.200			

TANTALUM IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	cal/°K gfw			Kcal/gfw			Log K_p
	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	
298.15	±.000	±.002	±.002	±.000			
1000	±.001	±.002	±.003	±.000			
2000	±.002	±.003	±.003	±.001			
3000	±.006	±.004	±.003	±.004			
4000	±.012	±.006	±.004	±.012			
5000	±.016	±.009	±.004	±.026			
6000	±.013	±.012	±.005	±.041			

21. Tantalum

The ideal monatomic gas thermodynamic functions of tantalum in Table XLIV were calculated from the energy levels listed by Moore[221] with the computer program discussed in section III-D. Uncertainty estimates are summarized on the back of the table.

22. Technetium

The ideal monatomic gas thermodynamic functions of technetium in Table XLV were calculated from the energy levels listed by Moore[221] with the computer program discussed in section III-D. Uncertainty estimates are summarized on the back of the table.

gfw = 99 (Isotope of Longest Known Half-Life)

T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal/°K gfw			Kcal/gfw			
0	0.000	0.000	Infinite				Infinite
298.15	4.970	43.250	43.250	0.000			
300	4.970	43.280	43.250	0.009			
400	4.999	44.713	43.445	0.507			
500	5.106	45.838	43.815	1.012			
600	5.328	46.787	44.233	1.532			
700	5.660	47.632	44.659	2.081			
800	6.060	48.413	45.080	2.667			
900	6.477	49.151	45.492	3.294			
1000	6.863	49.854	45.893	3.961			
1100	7.184	50.524	46.284	4.664			
1200	7.424	51.160	46.664	5.395			
1300	7.581	51.761	47.033	6.146			
1400	7.663	52.326	47.391	6.909			
1500	7.683	52.856	47.738	7.677			
1600	7.657	53.351	48.074	8.444			
1700	7.597	53.814	48.398	9.207			
1800	7.517	54.246	48.711	9.963			
1900	7.426	54.650	49.013	10.710			
2000	7.332	55.028	49.304	11.448			
2100	7.241	55.384	49.585	12.176			
2200	7.156	55.718	49.857	12.896			
2300	7.080	56.035	50.118	13.608			
2400	7.015	56.335	50.371	14.313			
2500	6.961	56.620	50.615	15.011			
2600	6.918	56.892	50.852	15.705			
2700	6.887	57.153	51.080	16.395			
2800	6.866	57.403	51.302	17.083			
2900	6.856	57.643	51.516	17.769			
3000	6.854	57.876	51.724	18.454			
3100	6.860	58.101	51.926	19.140			
3200	6.874	58.319	52.123	19.827			
3300	6.894	58.530	52.314	20.515			
3400	6.920	58.737	52.500	21.206			
3500	6.950	58.938	52.681	21.899			
3600	6.984	59.134	52.857	22.596			
3700	7.021	59.326	53.030	23.296			
3800	7.061	59.513	53.198	24.000			
3900	7.102	59.697	53.362	24.708			
4000	7.144	59.878	53.523	25.420			
4100	7.188	60.055	53.680	26.137			
4200	7.231	60.228	53.834	26.858			
4300	7.275	60.399	53.984	27.583			
4400	7.318	60.567	54.132	28.313			
4500	7.361	60.732	54.277	29.047			
4600	7.403	60.894	54.419	29.785			
4700	7.444	61.054	54.558	30.528			
4800	7.484	61.211	54.695	31.274			
4900	7.522	61.366	54.830	32.024			
5000	7.559	61.518	54.962	32.778			
5100	7.594	61.668	55.092	33.536			
5200	7.628	61.816	55.220	34.297			
5300	7.660	61.961	55.346	35.061			
5400	7.691	62.105	55.470	35.829			
5500	7.720	62.246	55.592	36.600			
5600	7.748	62.386	55.712	37.373			
5700	7.774	62.523	55.830	38.149			
5800	7.798	62.658	55.947	38.928			
5900	7.821	62.792	56.062	39.709			
6000	7.842	62.923	56.175	40.492			

TECHNETIUM IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	cal/°K gfw			Kcal/gfw			
	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	±.000	±.002	±.002	±.000			
1000	±.001	±.002	±.002	±.000			
2000	±.001	±.003	±.003	±.001			
3000	±.001	±.003	±.003	±.001			
4000	±.001	±.003	±.003	±.002			
5000	±.001	±.003	±.003	±.002			
6000	±.001	±.003	±.003	±.003			

23. Titanium

Prior to the publication of the JANAF Thermochemical Panel Interim Tables,[75] an analysis of the available basic data on titanium had been made on the present project. Since the results of the two analyses were in very close agreement, the values of the former analysis were accepted for the sake of compatibility and consistency with the addition of uncertainty limits from the new analysis. The following summary shows the extent of agreement of important quantities:

Quantity	Units	JANAF Table Value[75]	Avco RAD Analysis
T_t	°K	1155	1154
ΔH_t	Kcal/gfw	0.950	0.943
Melting Point	°K	1950	1945 ± 10
ΔH_m	Kcal/gfw	3.7	4.0 ± 0.5
S^o_{298}	e.u.	7.33	7.334
ΔH_v	Kcal/gfw	102.5*	
Boiling Point	°K	3550	---
ΔH^o_{s298}	Kcal/gfw	112.49	112.794

*Taken from monatomic gas table and rounded off.

a. Selection of Condensed-Phase Data

1) Crystal structure and solid-state transition

Titanium exists in two crystalline modifications.[57] The form stable at ordinary temperatures is close-packed hexagonal. This undergoes a transition[325,326] to the body-centered cubic form at about 1155° K. Hansen and Anderko[213] have reported a transition point value of 1158° K and Kothen[266] has reported a value of 1154° K for it.

The 1155° K value used in the JANAF tables for this transition point was adopted for the present work.

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[325] Edwards, J. W., H. L. Johnston, and W. E. Ditmars, J. Am. Chem. Soc. 73, 4729 (1951).

[326] McQuillan, A. D. Proc. Roy. Soc. (London) A204, 309 (1950).

*Taken from monatomic gas table and rounded off.

2) Melting point

There were many reported melting points for titanium. The recent compilation of Goldsmith et al[277] listed five references with an average recommended value of 1944° K. Stull and Sinke[77] chose 1950° ± 20° K. Kelley[56] chose 1940° K which is based on the work of Deardorff and Hayes.[327] A recent determination by Savitskii and Burkhanov[328] yielded a value of 1953° K.

The JANAF table value of 1950° K was accepted for the present work with an estimated uncertainty of ± 10° K.

3) Heat of transition

Golutvin[329] reported a solid-state heat of transition of 820 ± 20 cal/g atom while Schofield's value[330] of 830 ± 100 cal/g atom was quoted by Kubaschewski and Evans.[182] Stull and Sinke[77] chose a value of 950 cal/g atom, and Kothen's[266] measurements yielded a value of 943 cal/g atom. The agreement between the last two values is good. The JANAF table value of 950 cal/g atom was chosen for the present work.

4) Heat of fusion

There were no experimental data available for the heat of fusion of titanium. Values have been estimated on the assumption that the entropy of fusion has a value characteristic of the change from a body-centered cubic structure to the liquid. The following estimates have been reported.

ΔH_{fusion} (cal/g atom)	Reference
3700	Stull and Sinke[77]
4500 ± 500	Kubaschewski and Evans[182]
4460	Kelley[56]

[327] Deardorff, D. K. and E. T. Hayes, J. Metals 8, 509 (1956).

[328] Savitskii, E. M. and G. S. Burkhanov, Zhur. Neorg. Khim. 2, 2609 (1957).

[329] Golutvin, Y., Zhur. Fiz. Khim. 33, 1798 (1959); C. A. 54, 9479i (1960).

[330] Schofield, T. H., J. Inst. Metals 85, 68 (1956).

Some intermediate value like 4400 ± 600 cal/g atom would appear to be called for in a conservative evaluation. However, Kelley's value of 3700 cal/g atom was chosen to maintain agreement with the JANAF tables.

5) Low-temperature heat capacity and S°_{298}

Several sets of low-temperature heat capacity data, needed for the calculation of the entropy at 298.15° K, were summarized by Beckett *et al.*[331]

S°_{298} (e.u.)	Reference
7.32	Beckett *et al*[331]
7.33 ± 0.02	Stull and Sinke[77] and Kothen and Johnston[333]
7.334	Kothen[266]
7.37 ± 0.02	Clusius and Franzosini[332]

The recent work of Clusius and Franzosini compared well with the earlier determinations of Kothen,[266] and Kothen and Johnston.[333] The value for S°_{298} chosen in the present work was 7.330, and the value for $H^\circ_{298}-H^\circ_0$ was 1150 cal/mole, in agreement with those of the JANAF tables.

6) High-temperature heat capacity

Heat capacity measurements above room temperature have been made by several investigators.[266, 334, 335, 337, 338] From Goldsmith's[277] plot ot these data, it could be seen that the results of Kothen[266] and Scott[336] agree near the transition point, whereas those of Loewen[335] and Rea[334] appeared to be high. Kothen's[333] data also agree in this range with those of Jaeger *et al.*[337, 338]

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[331] Beckett, C. *et al*, Preliminary Report on the Thermodynamic Properties of Selected Light-Element Compounds, Nat. Bur. Stds, Rept. 6645 (1 January 1960); Amended (1 April 1960).

[332] Clusius, K. and P. Franzosini, Z. Physik. Chem. neue Folge 16, 194 (1958).

[333] Kothen, C. W. and H. L. Johnston, J. Am. Chem. Soc. 75, 3101 (1953).

[334] Rea, J. A., The Construction of a Furnace Calorimeter and the Evaluation of a Method of Thermal Analysis for Obtaining the Specific Heat of Solids at High Temperatures, M. S. Thesis, Oklahoma A and M, Stillwater (1953).

[335] Loewen, E. G., Trans. Am. Soc. Mech. Engrs. 78, 667 (1956).

[336] Scott, J. L., A Calorimeter Investigation of Zirconium, Titanium, and Zirconium Alloys from 60° to 960°C, Oak Ridge, Rept. ORNL-2328, AD-138-838. (1957)

[337] Jaeger, F. M., F. Rosenbohm, and R. Fonteyne, Proc. Acad. Sci. (Amsterdam) 39, 442 (1936).

[338] Jaeger, F. M., E. Rosenbohm, and R. Fonteyne, Rec. trav. chim. 55, 615 (1936).

The heat capacities beyond 1476° K used in the JANAF tables were accepted for the present work with some reservations since Kothen's[333] value of 10.47 cal/g atom at 1900° K was somewhat higher and his data at lower temperatures appeared to be good. Additional measurements on titanium at high temperatures therefore appeared to be desirable, and this was included in the work in Phase III of the project.

7) Heat of sublimation

Vapor pressure measurements have been reported by Edwards, Johnston, and Ditmars,[339] Blocker and Campbell,[340] Carpenter and Mair,[341] and Carpenter and Reavell.[342] Edwards et al[339] reported a heat of sublimation at 0° K of $\Delta H^\circ_{s0} = 112,763 \pm 83$ cal/mole. The last authors have corrected the work of the other investigators to obtain values of ΔH°_{s0} equal to 112,167 and 111,497 cal/mole. The JANAF table value of $\Delta H^\circ_{s298} = 112,490$ cal/mole was adopted.

8) The liquid heat capacity

The value of C°_p (liquid) = 8.000 cal/°K mole used in the JANAF tables for liquid titanium was adopted.

b. Calculations for Reference-State Tables

Thermodynamic function values from the JANAF tables for the reference state of titanium were adopted for Table XLVI with the addition of uncertainty estimates and extra entries to define discontinuities at transformations. Interpolations required for the extra entries were made by means of the Lagrangian interpolation formula[343] to assure accuracy in the third decimal place. The uncertainty calculations, summarized on the back of the table, were made by the methods described in section III-G.

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[339] Edwards, J. W., H. L. Johnston, and W. E. Ditmars, J. Am. Chem. Soc. 75, 2467 (1953).

[340] Blocker, J. M. and I. E. Campbell, J. Am. Chem. Soc. 71, 4040 (1949).

[341] Carpenter, L. G. and W. N. Mair, Proc. Phys. Soc. (London) 64B, 57 (1951).

[342] Carpenter, L. G. and F. R. Reavell, Nature 163, 527 (1949).

[343] Sokolnikoff, I. S. and E. S. Sokolnikoff, Higher Mathematics for Engineers and Physicists, McGraw-Hill, N. Y. (1941).

TABLE XLVI

TITANIUM | REFERENCE STATE | Ti

Reference State for Calculating ΔH_f°, ΔF_f°, and $\text{Log } K_p$: Solid from 298.15° to 1950°K, Liquid from 1950° to 3550°K, Gas from 3550° to 6000°K.

gfw = 47.90 | $T_t(l)$ = 1155°K | m.p. = 1950° ± 10°K | b.p. = 3550° ± 150°K

T, °K	cal/°K gfw C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	Kcal/gfw $H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	$\text{Log } K_p$
0	0.000	0.000	Infinite	-1.150			
298.15	5.970	7.330	7.330	0.000			
300	5.980	7.367	7.330	0.011			
400	6.360	9.147	7.570	0.631			
500	6.620	10.595	8.035	1.280			
600	6.840	11.822	8.566	1.953			
700	7.020	12.890	9.109	2.647			
800	7.180	13.838	9.642	3.357			
900	7.330	14.693	10.157	4.082			
1000	7.470	15.472	10.650	4.822			
1100	7.600	16.190	11.121	5.576			
1155	7.667	16.563	11.372	5.996			
1155	7.667	17.385	11.372	6.946			
1200	7.720	17.679	11.603	7.292			
1300	7.840	18.302	12.094	8.070			
1400	7.950	18.887	12.559	8.860			
1500	8.060	19.439	12.999	9.660			
1600	8.160	19.963	13.418	10.471			
1700	8.260	20.460	13.818	11.292			
1800	8.360	20.935	14.200	12.123			
1900	8.460	21.390	14.567	12.964			
1950	8.510	21.610	14.745	13.388			
1950	8.000	23.507	14.745	17.088			
2000	8.000	23.710	14.966	17.489			
2100	8.000	24.101	15.392	18.289			
2200	8.000	24.473	15.796	19.089			
2300	8.000	24.829	16.181	19.889			
2400	8.000	25.169	16.549	20.689			
2500	8.000	25.496	16.900	21.489			
2600	8.000	25.809	17.237	22.289			
2700	8.000	26.111	17.560	23.089			
2800	8.000	26.402	17.871	23.889			
2900	8.000	26.683	18.170	24.689			
3000	8.000	26.954	18.458	25.489			
3100	8.000	27.217	18.736	26.289			
3200	8.000	27.470	19.005	27.089			
3300	8.000	27.717	19.266	27.889			
3400	8.000	27.955	19.518	28.689			
3500	8.000	28.187	19.762	29.489			
3550	8.000	28.303	19.881	29.889			
3550	8.068	57.162	19.881	132.346			
3600	8.137	57.275	20.400	132.751			
3700	8.274	57.500	21.400	133.571			
3800	8.408	57.723	22.353	134.405			
3900	8.539	57.943	23.262	135.253			
4000	8.666	58.160	24.132	136.113			
4100	8.790	58.376	24.965	136.986			
4200	8.910	58.589	25.763	137.871			
4300	9.026	58.800	26.529	138.768			
4400	9.137	59.009	27.265	139.676			
4500	9.244	59.216	27.972	140.595			
4600	9.346	59.420	28.654	141.524			
4700	9.443	59.622	29.310	142.464			
4800	9.535	59.822	29.944	143.413			
4900	9.623	60.019	30.556	144.371			
5000	9.706	60.214	31.147	145.337			
5100	9.784	60.407	31.719	146.312			
5200	9.857	60.598	32.272	147.294			
5300	9.926	60.787	32.809	148.283			
5400	9.990	60.973	33.328	149.279			
5500	10.050	61.157	33.833	150.281			
5600	10.105	61.338	34.322	151.289			
5700	10.155	61.517	34.798	152.302			
5800	10.202	61.694	35.260	153.320			
5900	10.245	61.869	35.710	154.342			
6000	10.284	62.042	36.147	155.368			

TITANIUM REFERENCE STATE

SUMMARY OF UNCERTAINTY ESTIMATES

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	± .050	± .020	±.020	± .000			
1000	± .500	± .346	±.157	± .189			
1155	± .500	± .418	±.188	± .266			
1155	± .500	± .504	±.188	± .366			
1950	±1.000	± .896	±.403	± .962			
1950	±1.000	±1.152	±.403	±1.462			
2000	±1.000	±1.177	±.421	±1.512			
3000	±2.000	±1.785	±.781	±3.012			
3550	±2.000	±2.121	±.963	±4.112			
3550	±2.000	± .003	±.284	±1.002			
4000	± .002	± .003	±.253	±1.002			
5000	± .005	± .003	±.203	±1.003			
6000	± .010	± .003	±.170	±1.004			

1) Uncertainties in C_p^o

Uncertainties in C_p^o values were estimated from an examination of the following available data and derived points:

Source	C_p^o in cal/g atom °K					
	298° K	1000° K (α)	1155° K (α)	1155° K (β)	1950° K (β)	1950° K (ℓ)
JANAF Tables	5.970	7.47	7.67	7.67	8.51	8.00
Goldsmith et al[277]	5.987	7.66	8.14	7.18	10.77	
Kelley[56]	6.00	7.77	8.16	7.50	7.50	8.00
Kothen[266]	5.976	7.96	8.40	7.14	(10.77)*	
Golutvin[329]	4.783	8.435		7.968	(7.968)**	
Clusius and Franzosini[332]	5.998					

* Kothen[266] reported a value of 10.47 at 1900° K. This was extrapolated for the value at 1950° K. Goldsmith's[277] data were based on Kothen's[266] determinations.

**Golutvin[329] reported a value of 7.968 for the range from 1155° to 1400° K.

The following are the values adopted for the uncertainties in cal/ °K mole:

Temp(° K)	δC_p^o	Temp(° K)	δC_p^o
298	± 0.05	2000	± 1.0
1000	± 0.5	3000	± 2.0
1155 (α)	± 0.5	3550	± 2.0
1155 (β)	± 0.5	4000(v)	± 0.002
1950 (β)	± 1.0	5000(v)	± 0.005
1950 (ℓ)	± 1.0	6000(v)	± 0.010

2) Uncertainties in ($H_T^o - H_{298}^o$)

As explained in section III-G, average values of δC_p^o over the appropriate temperature ranges were calculated from the δC_p^o data as described just above, multiplied by the temperature interval, and summed cumulatively to obtain the uncertainties in ($H_T^o - H_{298}^o$) in Table XLVI up to the boiling point.

Above the boiling point, the equation used for calculating uncertainties was

$$\delta(H_T^o - H_{298}^o)_{(1)} = \delta \Delta H_{298}^o + \delta(H_T^o - H_{298}^o)_{(2)} , \qquad (158)$$

where subscript (1) = gas referred to solid at 298.15° K, and subscript (2) = gas referred to gas at 298.15° K.

It is evident from this equation that the uncertainty in ΔH_{298}^o contributes nearly all the total uncertainty in the gas enthalpy function of titanium because the last term on the right is very small.

3) Uncertainty in entropy

The equations used in calculating the uncertainty in S_T^o for condensed phases were discussed in section III-G. The mean errors in specific heat values for titanium presented in section IV-A23b(1) above were used for the numerical computations. For the gas phase above the boiling point, the errors in S_T^o were taken from the machine calculation for the ideal monatomic gas described in section IV-A23c below.

4) Uncertainty in free-energy function

The method used for the calculation of the uncertainty in the free-energy function of the condensed phases was also discussed earlier in section III-G of this report. The uncertainties in the free-energy function of the gas phase were also taken from the machine computation for the ideal monatomic gas described in section IV-A23c below.

The uncertainty estimates for the free-energy function of the condensed phases obtained in this work were larger than those reported by Hultgren et al:[76]

TABLE XLVII

TITANIUM — IDEAL MONATOMIC GAS — Ti

Reference State for Calculating ΔH_f°, ΔF_f°, and $\text{Log } K_p$: Solid from 298.15° to 1950°K, Liquid from 1945° to 3500°K, Gas from 3500° to 6000°K.

gfw = 47.90 | $T_t(I)$ = 1155°K | m.p. = 1950° ± 10°K | b.p. = 3550° ± 150°K

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-1.802	111.838	111.838	Infinite
298.15	5.838	43.068	43.068	0.000	112.490	101.835	-74.643
300	5.831	43.104	43.068	0.011	112.490	101.769	-74.135
400	5.522	44.735	43.293	0.577	112.476	98.201	-53.652
500	5.344	45.946	43.707	1.120	112.330	94.654	-41.371
600	5.237	46.911	44.164	1.648	112.185	91.132	-33.193
700	5.170	47.712	44.615	2.168	112.011	87.636	-27.360
800	5.128	48.400	45.046	2.683	111.816	84.167	-22.992
900	5.104	49.002	45.453	3.194	111.602	80.724	-19.602
1000	5.095	49.539	45.835	3.704	111.372	77.305	-16.894
1100	5.106	50.025	46.194	4.214	111.128	73.909	-14.684
1155	5.118	50.275	46.383	4.496	110.990	72.052	-13.633
1155	5.118	50.275	46.383	4.496	110.040	72.052	-13.633
1200	5.132	50.471	46.532	4.726	109.924	70.574	-12.853
1300	5.176	50.883	46.851	5.241	109.661	67.306	-11.315
1400	5.237	51.269	47.153	5.762	109.392	64.057	-9.999
1500	5.313	51.633	47.440	6.289	109.119	60.829	-8.862
1600	5.403	51.978	47.713	6.825	108.844	57.619	-7.870
1700	5.506	52.309	47.974	7.370	108.568	54.425	-6.996
1800	5.616	52.627	48.223	7.926	108.293	51.248	-6.222
1900	5.736	52.934	48.463	8.494	108.020	48.087	-5.531
1950	5.799	53.084	48.580	8.782	107.884	46.512	-5.213
1950	5.799	53.084	48.580	8.782	104.184	46.512	-5.213
2000	5.863	53.231	48.694	9.074	104.075	45.033	-4.921
2100	5.995	53.520	48.917	9.667	103.868	42.087	-4.380
2200	6.131	53.802	49.133	10.273	103.674	39.150	-3.889
2300	6.269	54.078	49.342	10.893	103.494	36.222	-3.442
2400	6.411	54.348	49.545	11.527	103.328	33.299	-3.032
2500	6.553	54.612	49.742	12.175	103.176	30.386	-2.656
2600	6.698	54.872	49.934	12.837	103.038	27.475	-2.309
2700	6.843	55.127	50.122	13.514	102.915	24.571	-1.989
2800	6.988	55.379	50.305	14.206	102.807	21.672	-1.691
2900	7.134	55.627	50.485	14.912	102.713	18.776	-1.415
3000	7.281	55.871	50.660	15.633	102.634	15.883	-1.157
3100	7.427	56.112	50.832	16.368	102.569	12.994	-0.916
3200	7.571	56.350	51.001	17.118	102.519	10.102	-0.690
3300	7.715	56.585	51.166	17.882	102.483	7.218	-0.478
3400	7.857	56.818	51.329	18.661	102.462	4.328	-0.278
3500	7.998	57.048	51.489	19.454	102.455	1.443	-0.090
3550	8.068	57.162	51.569	19.856	102.458	0.009	0.001
3550	8.068	57.162	51.569	19.856			
3600	8.137	57.275	51.647	20.261			
3700	8.274	57.500	51.802	21.081			
3800	8.408	57.722	51.955	21.915			
3900	8.539	57.942	52.106	22.763			
4000	8.666	58.160	52.254	23.623			
4100	8.790	58.376	52.401	24.496			
4200	8.910	58.589	52.546	25.381			
4300	9.026	58.800	52.689	26.277			
4400	9.137	59.009	52.830	27.186			
4500	9.244	59.215	52.970	28.105			
4600	9.346	59.419	53.108	29.034			
4700	9.443	59.621	53.244	29.974			
4800	9.535	59.821	53.379	30.923			
4900	9.623	60.019	53.513	31.881			
5000	9.706	60.214	53.645	32.847			
5100	9.784	60.407	53.775	33.822			
5200	9.857	60.598	53.905	34.804			
5300	9.926	60.786	54.033	35.793			
5400	9.990	60.972	54.160	36.789			
5500	10.050	61.156	54.285	37.791			
5600	10.105	61.338	54.509	38.798			
5700	10.156	61.517	54.533	39.812			
5800	10.202	61.694	54.654	40.829			
5900	10.245	61.869	54.775	41.852			
6000	10.284	62.041	54.895	42.878			

TITANIUM IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal/gfw)	ΔH_f° (Kcal/gfw)	ΔF_f° (Kcal/gfw)	Log K_p
298.15	±.000	±.002	±.003	±.000	±1.000	±1.007	±.738
1000	±.001	±.002	±.003	±.001	±1.190	±1.160	±.253
1155	±.001	±.002	±.003	±.001	±1.267	±1.220	±.230
1155	±.001	±.002	±.003	±.001	±1.367	±1.220	±.230
1950	±.001	±.002	±.003	±.001	±1.963	±1.791	±.200
1950	±.001	±.002	±.003	±.001	±2.463	±1.791	±.200
2000	±.001	±.002	±.003	±.001	±2.513	±1.848	±.201
3000	±.001	±.003	±.003	±.002	±4.014	±3.352	±.244
3550	±.002	±.003	±.003	±.002	±5.114	±4.429	±.272
3550	±.002	±.003	±.003	±.002			
4000	±.002	±.003	±.002	±.002			
5000	±.005	±.003	±.003	±.003			
6000	±.010	±.003	±.004	±.004			

Source	298° K	1155° K	1950° K	3000° K
Hultgren[76]	± 0.02	± 0.11	± 0.13	± 0.23
This work	± 0.02	± 0.19	± 0.40	± 0.78

The difference between the estimates is attributable to the larger uncertainties assigned in this work to the heat capacity values of the solid and liquid at high temperatures because of the discrepancies discussed in section IV-A23b(1) above.

c. Ideal Monatomic Gas Calculations

The ideal monatomic gas functions in Table XLVII were calculated by the methods described in section III-D using the energy levels of Moore.[52] The results agreed well with those in the JANAF tables. For the sake of consistency between tabulations, values of the thermodynamic functions in the latter tables were adopted with the uncertainty limits from the present computation summarized on the back of the table. The JANAF table value of $H^{\circ}_{298} - H^{\circ}_{0}$ = 1,802 cal/mole for the gas was accepted herein.

24. Tungsten

a. Crystal Structure and Transition Temperatures

The stable form of solid tungsten at 25°C is the body-centered cubic crystal.[344-347] A face-centered cubic form has been reported to be produced by electrolysis of fused tungstates, but it reverts irreversibly to the body-centered form if heated above 700°C.[346] No true allotropes of tungsten have been observed.[348] The body-centered cubic form was therefore taken as the stable form from room temperature to the melting point in this work. The melting point adopted for tungsten is 3650° ± 30°K and the estimated standard boiling point is 5891° ± 275°K

b. Melting Point

The "best" value of the melting point of tungsten has been taken to be 3650°K in recent compilations.[76, 77, 349] Other reported values ranged from 3370° to 3660°K. These older values were reviewed by Smithells[345] and by Richert, Beckett, and Johnston.[283]

The heat of fusion had not been experimentally determined. Estimated values ranged from 3000 to about 8400 cal/gfw.[76, 77, 256] In the absence of conclusive experimental data, an estimated heat of fusion of 8395 cal/gfw was chosen for this compilation. This value is based on an assumed entropy of fusion of 2.3 e.u. An uncertainty of ± 1000 cal/gfw was arbitrarily assigned to the heat of fusion at the melting point.

c. Standard Heat of Sublimation at 298.15°K, ΔH°_{s298}

Vapor pressure measurements for solid tungsten have been reported by Jones, Langmuir and MacKay,[261] and by Zwikker.[350] A ΔH°_{s298} value of 202,770 cal/gfw was calculated with the vapor pressure values

[344] Jette, E.R. and F. Foote, J. Chem. Phys. 3, 605 (1935).

[345] Smithells, C.J., Tungsten, Chemical Publ.,N.Y. (1953).

[346] Kirk, R.E. and D.F. Othmer, Encyclopedia of Chemical Technology, Interscience Publ., N.Y. (1955).

[347] Pugh, J.W., Metals 10, 335 (1958).

[348] Charlton, M.G. and G.L. Davis, Nature 175, 131 (1955).

[349] Brewer, L., National Nuclear Energy Ser. IV-19B (L.L. Quill, ed.), Mc-Graw-Hill, N.Y. (1950), paper 3.

[350] Zwikker, C., Physica 5, 249 (1925).

of Jones and co-workers,[261] and the free-energy functions from the present compilation. A similar calculation with the vapor pressure data of Zwikker[350] over the same temperature range yielded a ΔH°_{s298} value of 203, 380 cal/gfw. On the basis of these two calculated values, the one chosen in the present work was 203, 100 ± 1800 cal/gfw.

d. Boiling Point

The boiling point of tungsten had not been experimentally determined.

Estimated and/or quoted values ranged from 5100° to 6970°K; e.g.,

5100 - 5200°K[256]

5400°K[182]

5800°K[77]

5808°K[76]

6970°K.[261]

The chosen ΔH°_{s298} value of 203, 100 ± 1800 cal/gfw and free-energy functions for the gas and condensed phases from the present compilation were used to calculate a standard boiling point of 5891° ± 275°K in the present work.

The heat of vaporization at the standard boiling point was then estimated from the value of ΔH°_{s298} and the enthalpy functions for the gaseous and condensed phases at the standard boiling temperature. The value thus calculated was 192, 265 ± 11, 400 cal/gfw.

In Table XLVIII are summarized the heats of transformation for the various phase changes of tungsten.

TABLE XLVIII

TRANSITION DATA FOR TUNGSTEN

Transition	Temperature (°K)	ΔH_t (cal/gfw)
solid ⟶ liquid	3650 ± 30	8395 ± 1000
liquid ⟶ gas	5891 ± 275	192, 265 ± 11, 400
solid ⟶ gas	298.15	203, 100 ± 1800

e. Thermodynamic Functions for Condensed Phases

Recent compilations of thermodynamic functions for tungsten include those of Stull and Sinke,[77] Hultgren,[76] and Kelley.[56] The compilations of Stull and Sinke[77] and Kelley[56] extend to only 3000°K, thereby only including data for the solid phase. None of these compilations takes into account the recent low-temperature heat capacity data of Clusius and Franzosini,[265] or the heat capacity values at high temperatures very recently reported by workers at the Union Carbide Corporation.[351]

f. Entropy and Enthalpy at 298.15°K

Kelley[56] has reported an S^o_{298} value of 8.04 ± 0.10 e.u. based on the heat capacity measurements of Lange[352] (26° to 92°K), and of Zwikker and Schmidt[353] (92° to 290°K). This value was used by Stull and Sinke.[77] It should be noted that the heat capacity values of Zwikker and Schmidt[353] scatter over a range of ± 10 percent. Hultgren[76] reported an S^o_{298} value of 7.95 ± 0.10 e.u. based on the C^o_p values of Waite, Craig, and Wallace,[354] and of Horowitz and Daunt[280] for temperatures ranging up to 20°K; the C^o_p data of Lange[352] and DeSorbo[355] up to 90°K; and the data of Zwikker and Schmidt[353] up to room temperature. DeSorbo[355] reported an S^o_{298} value of 8.2 ± 0.2 e.u. from his measured C^o_p values combined with the data of Waite, Craig, and Wallace,[354] and of Zwikker and Schmidt.[353] Clusius and Franzosini[265] had recently measured the heat capacity very accurately over the temperature range from 10° to 273°K and reported S^o_{298} to be 7.83 e.u. The latter value has been accepted in the present work and assigned an uncertainty of ± 0.05 e.u. Integration of the heat capacity data of Clusius and Franzosini leads to a value of $H^o_{298} - H^o_0$ of 1195 ± 5 cal/gfw.

[351] Schomaker, V., R.H. Crist and R. Lowrie, Union Carbide Corporation for Advanced Research Projects Agency, Contract DA-30-069-ORD-2787, Progress Report (31 December 1960).

[352] Lange, F., Z. Physik Chem. 110, 343 (1924).

[353] Zwikker, C. and G. Schmidt, Z. Physik 52, 668 (1928).

[354] Waite, T.R., R.S. Craig and W.E. Wallace, Phys. Rev. 104, 1240 (1956).

[355] DeSorbo, W., J. Phys. Chem. 62, 965 (1958).

g. Thermodynamic Functions above 298.15°K

Several investigators have reported C_p^o values for the range of room temperature and above.[87, 194, 269, 353, 356-359] Previous[56, 76, 77] compilers had given most weight to the work of Jaeger and Rosenbohm[357] and of Magnus and Holzmann[87], and then, used an extrapolation of these data up to high temperatures. However, comparison of the C_p^o values thus obtained with low-temperature measurements of Clusius and Franzosini,[265] and the high-temperature measurements of Schomaker, Crist, and Lowrie[351] (1300°K - 2500°K), leads to the conclusion that values of previous compilers[56, 76, 77] are too high near room temperature and too low at temperatures above 1300°K.

Accordingly, the values of Clusius and Franzosini[265] were extended so as to join smoothly with the values of Schomaker, Crist, and Lowrie[351] at 1300°K. These C_p^o values were included in the present tables. Above 1300°K, the C_p^o values fit equation (159),

$$C_p^o = 4.70 + 1.5 \times 10^{-3}T \; , \qquad (159)$$

which was used for extrapolation up to the melting point of 3650°K.

From 298.15° to 1300°K, values of $H_T^o - H_{298}^o$ and S_T^o were evaluated by graphical integration. Values of $-\left(\frac{F_T^o - H_{298}^o}{T}\right)$ were obtained from equation (108).

Above 1300°K to the melting point, S_T^o and $H_T^o - H_{298}^o$ values were calculated from equations (160) and 161).

$$H_T^o - H_{298}^o = 4.70T + 75 \times 10^{-5}T^2 - 1130 \; , \qquad (160)$$

$$S_T^o = 4.70 \ln T + 1.5 \times 10^{-3}T - 18.762 \; . \qquad (161)$$

The values of the constants of integration in the above equations were evaluated from the tabular values of S_T^o and $H_T - H_{298}^o$ at 1300°K. The free-energy function was then calculated as indicated above.

[356] Jaeger, F.M. and E. Rosenbohm, Proc. Acad. Sci. (Amsterdam) 30, 1069 (1927).

[357] Jaeger, F.M. and E. Rosenbohm, Proc. Acad. Sci. (Amsterdam) 33, 457 (1930).

[358] Magnus, A. and H. Danz, Ann. Phys. 8, 408 ([illegible]).

[359] Forsythe, W.E. and A. [illegible] Worthing, Astrophys. J. [illegible] 146 ([illegible]).

No experimental value of C_p^o for liquid tungsten had been published. The heat capacity of liquid tungsten was taken to be constant at 10.00 cal/°K gfw. This value was chosen from a comparison of the values used for chromium (9.4 cal/° K gfw), molybdenum (10.00 cal/° K gfw), and solid tungsten at the melting point (10.175 cal/°K gfw). Previous compilations have used an estimated value of 8.5 cal/°K gfw.[76, 77]

Entropy and enthalpy values for liquid tungsten were therefore calculated with equations (162) and (163), respectively.

$$S_T^o = 10 \ln T - 54.460 \,, \tag{162}$$

$$H_T^o - H_{298}^o = 10T - 2088 \,. \tag{163}$$

The values of the constants of integration in the above equations were evaluated from the tabular values of S_T^o and $H_T^o - H_{298}^o$ for liquid tungsten at the melting point. The free-energy function for liquid tungsten was calculated from these values of S_T^o and $H_T^o - H_{298}^o$ in the manner described in section III-G.

The reference state thermodynamic functions of tungsten are given in Table XLIX. Uncertainty estimates are summarized on the back of the table.

h. Thermodynamic Functions for the Gaseous Phase

Thermodynamic properties for the ideal monatomic gas were calculated using the spectroscopic energy levels listed by Moore.[221] Energy levels and J values not definitely established in these tables were estimated. The equations employed in these calculations have been discussed in two recent publications,[51, 75] and are summarized in section III-D. $H_{298}^o - H_0^o$ was calculated to be 1486 cal/mole.

The $\Delta H_f^o, \Delta F_f^o$, and $\log_{10} K_p$ functions of gaseous tungsten were calculated by means of equations (42), (43), and (44).

The ideal monatomic gas thermodynamic functions of tungsten are given in Table L. Uncertainty estimates are summarized on the back of the table.

i. Uncertainty in Condensed Phase Functions

Uncertainties in the condensed phase functions of tungsten were calculated by the methods described in section III-G.

TABLE XLIX

TUNGSTEN — REFERENCE STATE — W

Reference State for Calculating ΔH_f°, ΔF_f°, and $\mathrm{Log}\ K_p$: Solid from 298.15° to 3650°K, Liquid from 3650° to 5891°K, Gas from 5891° to 6000°K.

gfw = 183.86 — m.p. = 3650° ± 30°K — b.p. = 5891° ± 275°K

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	$\mathrm{Log}\ K_p$
0	0.000	0.000	Infinite	-1.195			
298.15	5.800	7.830	7.830	0.000			
300	5.810	7.866	7.830	0.011			
400	5.960	9.580	8.082	0.599			
500	6.040	10.901	8.501	1.200			
600	6.110	12.027	9.015	1.807			
700	6.180	12.955	9.496	2.421			
800	6.240	13.803	9.999	3.043			
900	6.300	14.523	10.444	3.671			
1000	6.360	15.209	10.906	4.303			
1100	6.430	15.799	11.305	4.943			
1200	6.520	16.382	11.724	5.589			
1300	6.650	16.888	12.082	6.248			
1400	6.800	17.386	12.442	6.921			
1500	6.950	17.860	12.788	7.608			
1600	7.100	18.313	13.119	8.311			
1700	7.250	18.748	13.437	9.028			
1800	7.400	19.167	13.744	9.761			
1900	7.550	19.571	14.040	10.508			
2000	7.700	19.962	14.326	11.271			
2100	7.850	20.342	14.605	12.048			
2200	8.000	20.710	14.873	12.841			
2300	8.150	21.069	15.135	13.648			
2400	8.300	21.419	15.389	14.471			
2500	8.450	21.761	15.638	15.308			
2600	8.600	22.095	15.879	16.161			
2700	8.750	22.423	16.116	17.028			
2800	8.900	22.744	16.347	17.911			
2900	9.050	23.059	16.573	18.808			
3000	9.200	23.368	16.794	19.721			
3100	9.350	23.672	17.011	20.648			
3200	9.500	23.971	17.224	21.591			
3300	9.650	24.266	17.433	22.548			
3400	9.800	24.556	17.638	23.521			
3500	9.950	24.842	17.840	24.508			
3600	10.100	25.125	18.039	25.511			
3650	10.175	25.265	18.137	26.017			
3650	10.000	27.565	18.137	34.412			
3700	10.000	27.701	18.265	34.912			
3800	10.000	27.968	18.517	35.912			
3900	10.000	28.227	18.762	36.912			
4000	10.000	28.481	19.003	37.912			
4100	10.000	28.727	19.236	38.912			
4200	10.000	28.968	19.465	39.912			
4300	10.000	29.204	19.690	40.912			
4400	10.000	29.434	19.909	41.912			
4500	10.000	29.658	20.122	42.912			
4600	10.000	29.878	20.332	43.912			
4700	10.000	30.093	20.537	44.912			
4800	10.000	30.304	20.739	45.912			
4900	10.000	30.510	20.936	46.912			
5000	10.000	30.712	21.130	47.912			
5100	10.000	30.910	21.319	48.912			
5200	10.000	31.104	21.506	49.912			
5300	10.000	31.295	21.689	50.912			
5400	10.000	31.482	21.869	51.912			
5500	10.000	31.665	22.045	52.912			
5600	10.000	31.845	22.218	53.912			
5700	10.000	32.022	22.388	54.912			
5800	10.000	32.196	22.556	55.912			
5891	10.000	32.352	22.706	56.822			
5891	9.682	64.988	22.706	249.087			
5900	9.688	65.003	22.770	249.174			
6000	9.753	65.166	23.475	250.146			

TUNGSTEN REFERENCE STATE

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	cal/°K gfw C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	Kcal/gfw $H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0				± .005			
298.15	± .100	± .050	± .050	± .000			
1000	± .500	± .410	± .200	± .210			
2000	± .500	± .760	± .410	± .710			
3000	±1.000	±1.060	± .570	±1.460			
3650	±1.500	±1.300	± .680	±2.270			
3650	±2.000	±1.580	± .680	±3.270			
4000	±2.000	±1.760	± .770	±3.970			
5000	±3.000	±2.320	±1.030	±6.470			
5891	±4.000	±2.890	±1.260	±9.590			
5891	± .007	± .005					
6000	± .007	± .005					

TABLE L

TUNGSTEN — IDEAL MONATOMIC GAS — W

Reference State for Calculating ΔH_f°, ΔF_f°, and $\text{Log}\,K_p$: Solid from 298.15° to 3650°K, Liquid from 3650° to 5891°K, Gas from 5891° to 6000°K.

gfw = 183.86 m.p. = 3650° ± 30°K b.p. = 5891° ± 275°K

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-1.486	202.809	202.809	Infinite
298.15	5.092	41.551	41.551	0.000	203.100	193.046	-141.500
300	5.097	41.583	41.551	0.009	203.098	192.983	-140.582
400	5.536	43.101	41.755	0.538	203.039	189.631	-103.604
500	6.297	44.413	42.158	1.128	203.028	186.272	-81.415
600	7.251	45.643	42.637	1.804	203.097	182.927	-66.628
700	7.218	46.835	43.152	2.578	203.257	179.541	-56.053
800	9.026	47.987	43.685	3.442	203.499	176.151	-48.120
900	9.577	49.085	44.224	4.375	203.804	172.697	-41.935
1000	9.856	50.111	44.762	5.348	204.145	169.244	-36.986
1100	9.904	51.054	45.292	6.338	204.495	165.714	-32.923
1200	9.788	51.912	45.809	7.324	204.835	162.197	-29.539
1300	9.569	52.687	46.308	8.292	205.144	158.607	-26.663
1400	9.298	53.387	46.789	9.236	205.415	155.015	-24.198
1500	9.008	54.018	47.251	10.151	205.643	151.407	-22.059
1600	8.721	54.590	47.692	11.038	205.827	147.784	-20.185
1700	8.451	55.111	48.113	11.896	205.968	144.153	-18.531
1800	8.206	55.587	48.515	12.729	206.068	140.513	-17.060
1900	7.987	56.025	48.899	13.538	206.130	136.870	-15.743
2000	7.797	56.429	49.266	14.327	206.156	133.220	-14.557
2100	7.635	56.806	49.616	15.098	206.150	129.576	-13.485
2200	7.500	57.158	49.951	15.855	206.114	125.930	-12.509
2300	7.391	57.489	50.271	16.599	206.051	122.286	-11.619
2400	7.306	57.801	50.579	17.334	205.963	118.646	-10.804
2500	7.243	58.098	50.874	18.061	205.853	115.010	-10.054
2600	7.201	58.381	51.157	18.783	205.722	111.379	-9.362
2700	7.179	58.653	51.430	19.502	205.574	107.752	-8.721
2800	7.173	58.913	51.692	20.220	205.409	104.132	-8.127
2900	7.184	59.165	51.946	20.937	205.229	100.520	-7.575
3000	7.209	59.409	52.190	21.657	205.036	96.909	-7.059
3100	7.247	59.646	52.427	22.380	204.832	93.310	-6.578
3200	7.297	59.877	52.656	23.107	204.616	89.718	-6.127
3300	7.357	60.103	52.878	23.839	204.391	86.130	-5.704
3400	7.426	60.323	53.094	24.578	204.157	82.552	-5.306
3500	7.503	60.540	53.304	25.325	203.917	78.974	-4.931
3600	7.586	60.752	53.508	26.079	203.668	75.413	-4.578
3650	7.630	60.857	53.608	26.460	203.543	73.631	-4.409
3650	7.630	60.857	53.608	26.460	195.148	73.631	-4.409
3700	7.675	60.961	53.706	26.842	195.030	71.969	-4.251
3800	7.769	61.167	53.900	27.615	194.803	68.647	-3.948
3900	7.866	61.370	54.089	28.396	194.584	65.325	-3.661
4000	7.965	61.570	54.274	29.188	194.376	62.016	-3.388
4100	8.067	61.768	54.454	29.989	194.177	58.704	-3.129
4200	8.169	61.964	54.630	30.801	193.989	55.401	-2.883
4300	8.273	62.157	54.803	31.623	193.813	52.116	-2.649
4400	8.376	62.349	54.973	32.456	193.644	48.818	-2.425
4500	8.478	62.538	55.139	33.298	193.486	45.522	-2.211
4600	8.580	62.726	55.301	34.151	193.339	42.242	-2.007
4700	8.680	62.911	55.461	35.014	193.202	38.963	-1.812
4800	8.778	63.095	55.619	35.887	193.075	35.674	-1.624
4900	8.874	63.277	55.773	36.770	192.958	32.399	-1.445
5000	8.968	63.457	55.925	37.662	192.850	29.125	-1.273
5100	9.059	63.636	56.074	38.563	192.751	25.852	-1.108
5200	9.148	63.812	56.221	39.473	192.661	22.584	-0.949
5300	9.234	63.988	56.366	40.393	192.581	18.312	-0.755
5400	9.317	64.161	56.509	41.320	192.508	16.043	-0.649
5500	9.397	64.333	56.650	42.256	192.444	12.771	-0.507
5600	9.474	64.503	56.788	43.199	192.387	9.509	-0.371
5700	9.548	64.671	56.925	44.150	192.338	6.242	-0.239
5800	9.619	64.838	57.060	45.109	192.297	2.975	-0.112
5891	9.682	64.988	57.181	45.987	192.265	0.000	0.000
5891	9.682	64.988	57.181	45.987			
5900	9.688	65.003	57.193	46.074			
6000	9.753	65.166	57.325	47.046			

TUNGSTEN IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	±.000	±.002	±.002	±.000	±1.800	±1.820	±1.330
1000	±.001	±.003	±.003	±.001	±2.010	±2.000	± .440
2000	±.001	±.003	±.003	±.001	±2.510	±2.630	±..290
3000	±.001	±.003	±.003	±.002	±3.260	±3.520	± .260
3650	±.002	±.003	±.003	±.002	±4.070	±4.290	± .260
3650	±.002	±.003	±.003	±.002	±5.070	±4.290	± .260
4000	±.003	±.003	±.003	±.003	±5.770	±4.890	± .270
5000	±.006	±.004	±.003	±.007	±8.280	±6.970	± .300
5891	±.007	±.005	±.003	±.012	±1.140	±9.240	± .340
5891	±.007	±.005	±.003	±.012			
6000	±.007	±.005	±.003	±.013			

1) Heat capacity

Graphical intercomparison of reported C_p^o values for solid tungsten led to the following choices of uncertainties:

± 0.1 cal/°K gfw at 298.15°K

± 0.5 cal/°K gfw at 1000°K

± 0.5 cal/°K gfw at 2000°K

± 1.0 cal/°K gfw at 3000°K

± 1.5 cal/°K gfw at m.p. (3650°K).

The heat capacity of liquid tungsten had apparently never been experimentally measured; therefore, a rather large overall uncertainty was arbitrarily assigned to the estimated value. Particular uncertainties assigned were as follows:

± 2.0 cal/°K gfw at m.p. (3650°K)

± 2.0 cal/°K gfw at 4000°K

± 3.0 cal/°K gfw at 5000°K

± 4.0 cal/°K gfw at b.p. (5891°K).

2) Entropy

Uncertainties in entropy values were calculated from assigned uncertainties in C_p^o values, and assigned uncertainties for heats of transitions by the method described in section III-G. Equation (149) was used at transitions.

3) Free energy

The uncertainties in free-energy function were calculated from uncertainties in S_T^o and $H_T^o - H_{298}^o$ by means of equation (120).

j. Uncertainties in Gas-Phase Functions

Uncertainties in the ideal gas thermodynamic functions at the specified temperatures were computed as explained in section III-D2. The uncertainties in ΔH_f^o, ΔF_f^o, and $\log_{10} K_p$ were calculated by means of equations (46) (47), and (48).

k. Other Reference Pertaining to the Thermodynamics of Tungsten

Heat capacity measurements at low temperatures have also been reported and discussed by Boosz,[278] Wolcott,[204] and Rayne.[279] Heat capacities at high temperatures have also been reported by Southern Research Insititute[29] workers.

The vapor pressure data of Jones, Langmuir, and MacKay[261] were re-calculated from the original data of Langmuir.[360] The vapor pressure values reported by van Liempt[282] are smoothed values from Langmuir's original work.[360]

Useful annotated bibliographies on tungsten were those of Goodwin and Ayton,[209] and of Richert, Beckett, and Johnston.[283]

[360] Langmuir, I., Phys. Rev. 2, 450 (1913).

TABLE LI
IDEAL MONATOMIC GAS

gfw = 50.95

T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal/°K gfw			Kcal/gfw			
0	0.000	0.000	Infinite	-			Infinite
298.15	6.217	43.546	43.546	0.000			
300	6.209	43.584	43.546	0.011			
400	5.891	45.321	43.785	0.615			
500	5.783	46.621	44.227	1.197			
600	5.804	47.676	44.717	1.775			
700	5.875	48.576	45.205	2.359			
800	5.949	49.365	45.677	2.951			
900	6.003	50.069	46.127	3.548			
1000	6.032	50.704	46.553	4.150			
1100	6.038	51.279	46.957	4.754			
1200	6.026	51.804	47.339	5.357			
1300	6.003	52.285	47.702	5.959			
1400	5.974	52.729	48.045	6.558			
1500	5.943	53.140	48.371	7.154			
1600	5.913	53.523	48.681	7.746			
1700	5.887	53.881	48.977	8.336			
1800	5.867	54.216	49.259	8.924			
1900	5.853	54.533	49.528	9.510			
2000	5.846	54.833	49.786	10.095			
2100	5.848	55.119	50.033	10.680			
2200	5.858	55.391	50.270	11.265			
2300	5.877	55.652	50.499	11.851			
2400	5.904	55.902	50.719	12.440			
2500	5.940	56.144	50.931	13.033			
2600	5.985	56.378	51.136	13.629			
2700	6.038	56.605	51.334	14.230			
2800	6.099	56.825	51.526	14.837			
2900	6.168	57.040	51.713	15.450			
3000	6.245	57.251	51.894	16.070			
3100	6.328	57.457	52.070	16.699			
3200	6.418	57.659	52.242	17.336			
3300	6.515	57.858	52.409	17.983			
3400	6.617	58.054	52.572	18.639			
3500	6.723	58.248	52.731	19.306			
3600	6.835	58.438	52.887	19.984			
3700	6.950	58.627	53.040	20.673			
3800	7.068	58.814	53.189	21.374			
3900	7.188	58.999	53.336	22.087			
4000	7.311	59.183	53.480	22.812			
4100	7.435	59.365	53.621	23.549			
4200	7.560	59.546	53.760	24.299			
4300	7.685	59.725	53.897	25.061			
4400	7.810	59.903	54.031	25.836			
4500	7.935	60.080	54.164	26.623			
4600	8.058	60.256	54.294	27.423			
4700	8.180	60.430	54.423	28.235			
4800	8.300	60.604	54.550	29.059			
4900	8.419	60.776	54.675	29.895			
5000	8.534	60.947	54.799	30.743			
5100	8.648	61.118	54.921	31.602			
5200	8.758	61.287	55.042	32.472			
5300	8.866	61.454	55.161	33.353			
5400	8.970	61.621	55.279	34.245			
5500	9.071	61.787	55.396	35.147			
5600	9.169	61.951	55.512	36.059			
5700	9.264	62.114	55.626	36.981			
5800	9.354	62.276	55.739	37.912			
5900	9.442	62.437	55.852	38.852			
6000	9.526	62.596	55.963	39.800			

VANADIUM IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	cal/°K gfw			Kcal/gfw			Log K_p
	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	
298.15	±.000	±.002	±.003	±.000			
1000	±.000	±.002	±.003	±.000			
2000	±.000	±.003	±.003	±.001			
3000	±.001	±.003	±.003	±.001			
4000	±.001	±.003	±.003	±.002			
5000	±.002	±.003	±.003	±.003			
6000	±.003	±.004	±.003	±.005			

25. Vanadium

The ideal monatomic gas thermodynamic functions of vanadium in Table LI were calculated from the energy levels listed by Moore[52] with the computer program discussed in section III-D. Uncertainty estimates are summarized on the back of the table.

26. Zirconium

The reference state thermodynamic functions of zirconium are given in Table LII. Uncertainty estimates are summarized on the back of the table.

a. Condensed Phase Data

1) Crystalline forms and range of stability

Elemental zirconium is known to exist in two different crystalline modifications.[361] At room temperature, the stable modification has a hexagonal, close-packed structure which persists up to 1135°K. Above this temperature, the body-centered cubic structure is the stable one.

2) Transition temperatures

a) Solid state transition

Miller[361] accepted 1135°K (862°C) as the solid-state transition temperature, Hansen and Anderko[213] have used a value of 1138°K (865°C), Skinner[362] found a value of 1143°K, and Kelley[56] adopted a value of 1135°K. The last value is the one used in the present tabulation with an uncertainty of ± 10°K to include all the above values.

b) Melting point

For pure, hafnium-free zirconium, Miller[361] tabulated melting points of 2118°K (1845°C), based on the work of Adenstedt[219] and 2128°± 15°K (1855°± 15°C), from the work of Deardorff and Hayes.[327] Oriani and Jones[363] obtained a melting point of 2141°K. Hultgren *et al*[76] interpreted the last results to obtain a melting point of 2125°K. The Hultgren *et al* value was accepted for the present compilation.

c) Boiling point

Accurate experimental determinations of the boiling point of zirconium appeared not to be available. Hultgren et al[76] have calculated a boiling point of 4688°K. Miller[361] reported a value of 3850°K (3577°C) based on the older work of Quill.[364]

[361] Miller, G., Zirconium, Academic Press, N.Y. (1957).

[362] Skinner, G.B., Ph.D. Thesis, Ohio State University (1951).

[363] Oriani, R.A. and T.S. Jones, Rev. Sci. Instr. 25, 248 (1954).

[364] Quill, L.L., The Chemistry and Metallurgy of Miscellaneous Materials, McGraw-Hill, N.Y. (1950).

TABLE LII

ZIRCONIUM — REFERENCE STATE — Zr

Reference State for Calculating ΔH_f°, ΔF_f°, and $\mathrm{Log}\ K_p$: Solid from 298.15° to 2125°K, Liquid from 2125° to 4743°K, Gas from 4743° to 6000°K.

gfw = 91.22 T_t = 1135° ± 10°K m.p. = 2125° ± 10°K b.p. = 4743° ± 165°K*

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-1.313			
298.15	6.001	9.290	9.290	0.000			
300	6.015	9.327	9.290	0.011			
400	6.556	11.141	9.533	0.643			
500	6.882	12.642	10.011	1.316			
600	7.125	13.920	10.559	2.016			
700	7.327	15.034	11.121	2.739			
800	7.508	16.025	11.674	3.481			
900	7.677	16.920	12.208	4.240			
1000	7.838	17.737	12.721	5.016			
1100	7.995	18.493	13.211	5.810			
1135	8.049	18.745	13.378	6.091			
1135	7.900	19.551	13.378	7.006			
1200	7.900	19.991	13.725	7.519			
1300	7.900	20.623	14.231	8.309			
1400	7.900	21.209	14.709	9.099			
1500	7.900	21.754	15.161	9.889			
1600	7.900	22.264	15.589	10.679			
1700	7.900	22.743	15.996	11.469			
1800	7.900	23.194	16.383	12.259			
1900	7.900	23.621	16.753	13.049			
2000	7.900	24.027	17.107	13.839			
2100	7.900	24.412	17.446	14.629			
2125	7.900	24.505	17.528	14.826			
2125	8.000	26.811	17.528	19.726			
2200	8.000	27.088	17.849	20.326			
2300	8.000	27.444	18.259	21.126			
2400	8.000	27.785	18.649	21.926			
2500	8.000	28.111	19.021	22.726			
2600	8.000	28.425	19.376	23.526			
2700	8.000	28.727	19.717	24.326			
2800	8.000	29.018	20.044	25.126			
2900	8.000	29.299	20.359	25.926			
3000	8.000	29.570	20.661	26.726			
3100	8.000	29.832	20.953	27.526			
3200	8.000	30.086	21.234	28.326			
3300	8.000	30.332	21.506	29.126			
3400	8.000	30.571	21.769	29.926			
3500	8.000	30.803	22.024	30.726			
3600	8.000	31.028	22.271	31.526			
3700	8.000	31.248	22.511	32.326			
3800	8.000	31.461	22.743	33.126			
3900	8.000	31.669	22.970	33.926			
4000	8.000	31.871	23.190	34.726			
4100	8.000	32.069	23.404	35.526			
4200	8.000	32.262	23.612	36.326			
4300	8.000	32.450	23.816	37.126			
4400	8.000	32.634	24.014	37.926			
4500	8.000	32.814	24.208	38.726			
4600	8.000	32.989	24.397	39.526			
4700	8.000	33.161	24.581	40.326			
4743.34*	8.000	33.234	24.659	40.673			
4743.34	9.008	62.416	24.659	179.096			
4800	9.039	62.524	25.106	179.607			
4900	9.091	62.711	25.872	180.514			
5000	9.139	62.895	26.610	181.425			
5100	9.185	63.076	27.323	182.341			
5200	9.226	63.255	28.012	183.262			
5300	9.265	63.431	28.679	184.187			
5400	9.300	63.605	29.324	185.115			
5500	9.332	63.775	29.948	186.046			
5600	9.361	63.944	30.554	186.981			
5700	9.387	64.110	31.142	187.919			
5800	9.409	64.273	31.711	188.858			
5900	9.429	64.434	32.264	189.800			
6000	9.446	64.593	32.802	190.744			

*From change in sign of ΔF_f° of ideal gas.

ZIRCONIUM REFERENCE STATE

SUMMARY OF UNCERTAINTY ESTIMATES

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	± .050	± .040	± .040	± .000			
1000	± .500	± .123	± .065	± .058			
1135	± .500	± .185	± .077	± .123			
1135	± .500	± .273	± .077	± .223			
2000	±1.000	± .569	± .229	± .680			
2125	±1.000	± .625	± .251	± .796			
2125	±2.000	± .860	± .251	±1.296			
3000	±2.000	±1.550	± .535	±3.046			
4000	±2.000	±2.125	± .864	±5.046			
4743.34	±2.000	±2.465	±1.088	±6.532			
4743.34	± .002	± .004					
5000	± .002	± .004					
6000	± .001	± .004					

Kubaschewski and Evans[182] reported an approximate value of 5023°K (4750°C), and Stull and Sinke[77] obtained a value of 4650°K. From the data in the present compilation, a boiling point of 4743° ± 165°K was calculated and adopted.

3) Heats of transformation

a) Heat of transition

The following values had been reported for the solid-state heat of transition at 1135°K:

Heat of Transition (cal/mole)	Source
1040	Stull and Sinke[77]
920	Miller,[361] p. 151, based on Coughlin and King's work[365]
915	Kelley,[56] p. 209

In the present tabulation, Kelley's value of 915 cal/mole was accepted.

b) Heat of fusion

There were several estimates available for the heat of fusion of zirconium.

Heat of Fusion (cal/mole)	Source
5500	Miller,[361] p. 151, based on Quill [364]
4000	Stull and Sinke[77]
4890	Hultgren[76]

A value of 4900 cal/mole as recommended by Kelley was used for the heat of fusion of zirconium in the present tabulation.

[365]Coughlin, J.P. and E.G. King, J. Am. Chem. Soc. 73, 2032 (1951).

c) Heat of sublimation

The only vapor pressure measurements reported for zirconium were those of Skinner, Edwards, and Johnston.[366] Stull and Sinke[77] used these data to determine that ΔH°_{f298} = 146,000 cal/mole for the temperature range from 1949° to 2054°K assuming the condensation coefficient to be equal to unity. Hultgren et al[76] obtained a value of 145,760 cal/mole from the same data. Lewis et al[220] have tabulated a value of 146,000 ± 1000 cal/mole. The latter was accepted in the present compilation.

4) Heat capacity

a) Low-temperature data

Low-temperature heat capacity data have been reported by Skinner and Johnston[367] for the range from 14° to 300°K. Their data yield a standard state entropy of S°_{298} = 9.29 ± 0.04 e.u. Additional data have been reported by Todd[368] for the range from 51° to 298°K and by Burk, Estermann, and Friedberg[218] for the range from 15° to 200°K. The latter data agree within 1 percent with those of Skinner and Johnston,[367] which were accepted here since they cover a wider temperature range. The above value of the standard state entropy was also accepted. $H^\circ_{298} - H^\circ_0$ was taken to be 1313 cal/gfw.

b) High-temperature data

High-temperature heat capacity data for zirconium from various sources have been reviewed by Kelley.[56] His review included the recent work of Douglas and Victor.[369] Other sources of data were as follows:

[366] Skinner, G.B., J.W. Edwards, and H.L. Johnston, J. Am. Chem. Soc. 73, 174 (1951).

[367] Skinner, G.B. and H.L. Johnston, J. Am. Chem. Soc. 73, 4549 (1951).

[368] Todd, S.S., J. Am. Chem. Soc. 72, 2914 (1950).

[369] Douglas, T.B. and A.C. Victor, J. Research Nat. Bur. Stds. 61, 13 (1958).

TABLE LIII

ZIRCONIUM — IDEAL MONATOMIC GAS — **Zr**

Reference State for Calculating ΔH_f°, ΔF_f°, and $\mathrm{Log}\,K_p$: Solid from 298.15° to 2125°K, Liquid from 2125° to 4743°K, Gas from 4743° to 6000°K.

gfw = 91.22 — T_t = 1135° ± 10°K — m.p. = 2125° ± 10°K — b.p. = 4743° ± 165°K

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-1.629			Infinite
298.15	6.368	43.317	43.317	0.000	146.000		
300	6.375	43.356	43.317	0.012			
400	6.612	45.231	43.571	0.664			
500	6.594	46.707	44.056	1.326			
600	6.464	47.899	44.601	1.979			
700	6.316	48.884	45.144	2.618			
800	6.199	49.719	45.665	3.243			
900	6.133	50.445	46.157	3.859			
1000	6.121	51.090	46.619	4.472			
1100	6.156	51.675	47.052	5.085			
1135	6.182	51.912	47.230	5.350			
1135	6.182	51.912	47.230	5.350			
1200	6.226	52.213	47.460	5.704			
1300	6.320	52.715	47.845	6.331			
1400	6.428	53.188	48.210	6.969			
1500	6.542	53.635	48.557	7.617			
1600	6.655	54.061	48.888	8.277			
1700	6.764	54.468	49.204	8.948			
1800	6.866	54.857	49.507	9.629			
1900	6.960	55.231	49.799	10.321			
2000	7.047	55.590	50.080	11.021			
2100	7.128	55.936	50.350	11.730			
2125	7.148	56.020	50.416	11.909			
2125	7.148	56.020	50.416	11.909			
2200	7.204	56.269	50.612	12.447			
2300	7.276	56.591	50.865	13.171			
2400	7.345	56.902	51.110	13.902			
2500	7.413	57.203	51.348	14.640			
2600	7.481	57.496	51.578	15.384			
2700	7.549	57.779	51.803	16.136			
2800	7.618	58.055	52.021	16.894			
2900	7.688	58.323	52.234	17.659			
3000	7.760	58.585	52.441	18.432			
3100	7.833	58.841	52.644	19.212			
3200	7.908	59.091	52.841	19.999			
3300	7.984	59.335	53.034	20.793			
3400	8.061	59.575	53.223	21.595			
3500	8.139	59.810	53.408	22.405			
3600	8.217	60.040	53.589	23.223			
3700	8.294	60.266	53.767	24.049			
3800	8.371	60.448	53.941	24.882			
3900	8.447	60.707	54.111	25.723			
4000	8.522	60.922	54.279	26.571			
4100	8.595	61.133	54.443	27.427			
4200	8.666	61.341	54.605	28.290			
4300	8.735	61.546	54.764	29.160			
4400	8.802	61.747	54.921	30.037			
4500	8.865	61.946	55.075	30.921			
4600	8.926	62.141	55.226	31.810			
4700	8.984	62.334	55.375	32.706			
4800	9.039	62.524	55.522	33.607			
4900	9.091	62.711	55.667	34.514			
5000	9.139	62.895	55.810	35.425			
5100	9.185	63.076	55.950	36.341			
5200	9.226	63.255	56.089	37.262			
5300	9.265	63.431	56.226	38.187			
5400	9.300	63.605	56.361	39. 15			
5500	9.332	63.775	56.494	40.046			
5600	9.361	63.944	56.626	40.981			
5700	9.387	64.110	56.756	41.919			
5800	9.409	64.273	56.884	42.858			
5900	9.429	64.434	57.011	43.800			
6000	9.446	64.593	57.136	44.744			

ZIRCONIUM IDEAL MONATOMIC GAS

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	cal/°K gfw C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	Kcal/gfw $H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	±.001	±.002	±.003	±.000	±1.000		
1000	±.001	±.002	±.003	±.000			
1135	±.001	±.002	±.003	±.000			
1135	±.001	±.002	±.003	±.000			
2000	±.001	±.003	±.003	±.001			
2125	±.001	±.003	±.003	±.001			
2125	±.001	±.003	±.003	±.001			
3000	±.002	±.003	±.003	±.002			
4000	±.002	±.003	±.003	±.003			
5000	±.002	±.004	±.003	±.005			
6000	±.001	±.004	±.003	±.006			

Temperature Range (°K)	Reference
298-1371	Coughlin and King[370]
423-1273	Redmond and Lones[371]
363-1223	Scott[336]
294-1074	Jaeger and Veenstra[372]

The values chosen by Kelley were accepted herein, including his estimated value of C_p^o = 8.000 cal/gfw for the liquid.

c) Monatomic gas table

The ideal monatomic gas thermodynamic functions of zirconium in Table LIII were calculated from the energy levels listed by Moore[52] with the computer program described in section III-D Uncertainty estimates are summarized on the back of the table. $H^o_{298} - H^o_0$ was found to be 1,629 cal/mole for the ideal gas.

370 Coughlin, J.P. and E.G. King, J. Am. Chem. Soc. 72, 2262 (1950).

371 Redmond, R.F. and J. Lones, AEC, ORNL-1342 (1952).

372 Jaeger, F.M. and W.A. Veenstra, Rec. trav. chim. 53, 917 (1934).

B. COMPOUNDS

1. Beryllium Oxide (BeO)

a. Crystal Structure and Melting Point

Beryllium oxide has a hexagonal (wurtzite-type) structure at room temperature.[231] Jeffrey, Parry, and Mozzi[373] determined some of the structural details by X-ray analysis. The hexagonal structure appears to be thermally stable. Klein[374] found the thermal expansion of BeO to be isotropic up to at least 2025°K. The heat content measurements of Kandyba *et al*[375] from 1200°K to the melting point gave no indication of any solid-state transformation.

Recent reported values for the melting point of BeO have ranged from 2723° to 2843°K.[375-380] A melting point of 2820° ± 15°K[375] was selected for this compilation.

b. Thermodynamic Properties of Condensed Phases

1) Heat of fusion

Kandyba *et al*[375] made heat content measurements on solid and liquid BeO. From one heat content measurement on liquid BeO at 2840°K, the heat of fusion was calculated to be 15.440 Kcal/gfw. An uncertainty of ± 0.500 Kcal/gfw was assigned. The entropy of fusion was thus 5.475 ± .180 cal/°K gfw. The heat of fusion had been estimated to be 14 Kcal/gfw in the JANAF compilation,[75] and to be 17 Kcal/gfw (from an estimated entropy of fusion of 6.0 cal/°K gfw) by Erway and Seifert.[381]

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[373] Jeffrey, G., G. Parry, and R. Mozzi, J. Chem. Phys. 25, 1024 (1956).

[374] Klein, D., North American Aviation Co. Rept. NAA-SR-2542 (1958).

[375] Kandyba, V.V., P.B. Kantor, R.M. Krasovitskaya, and E.N. Fomichev, Doklady Akad. Nauk SSSR 131, 566 (1960).

[376] Ol'shanskii, Y., Doklady Akad. Nauk SSSR 59, 1105 (1948).

[377] Wartenberg, H. von and H. Werth, Z. anorg. u. allgem. Chem. 190, 178 (1930).

[378] Engberg, C. and E. Zehms, J. Am. Ceram. Soc. 42, 300 (1959).

[379] Wartenberg, H. von and H.J. Reusch, Z. anorg. Chem. 207, 1 (1932).

[380] Wartenberg, H. von, H.J. Reusch, and E. Saran, Z. anorg. Chem 230, 267 (1937).

[381] Erway, N.D. and R.L. Seifert, J. Electrochem. Soc. 98, 83 (1957).

2) Entropy and heat content at 298.15°K

Low-temperature heat capacity measurements of BeO made by Gunther[143] (76° to 85°K) and by Kelley[382] (55° to 292°K) were not in agreement. Kelley[139] gave S°_{298} as 3.37 ± 0.02 cal/°K gfw from his measurements. The National Bureau of Standards[78] joined the low-temperature data of Kelley[382] smoothly at 400°K with the unpublished high-temperature heat content measurements of Victor and Douglas and calculated S°_{298} to be 3.376 ± 0.050 cal/°K gfw. This value was adopted here. C°_p at 298.15°K was thereby changed from 6.07 cal/°K gfw as given by Kelley[139] to 6.105 cal/°K gfw. $H^\circ_{298} - H^\circ_0$ was taken as 686.6 cal/gfw from the National Bureau of Standards.[78]

3) High-temperature heat content

High-temperature heat content measurements on BeO have been made by Magnus and Danz[358] (293° to 1175°K), Nilson and Pettersson[383] (273° to 293°K), Victor and Douglas[78] (273° to 1200°K), and Kandyba et al[375] (1200° to 2840°K). The results of Magnus and Danz[358] were 0 to 1.5 percent higher than those of Victor and Douglas[78] over the temperature range of measurement. At 1200°K, Magnus and Danz[358] and Kandyba et al[375] were one percent higher and lower, respectively, than Victor and Douglas.[78] Equations representing heat content data from these three sources were:

a) Magnus and Danz[358] (298° to 1200°K in cal/gfw)

$$H^\circ_T - H^\circ_{298} = 8.45\,T + 2.00 \times 10^{-3}\,T^2 + 3.17 \times 10^5\,T^{-1} - 3700 . \quad (164)$$

b) Victor and Douglas[78] (298° to 1200°K in cal/gfw)

$$H^\circ_T - H^\circ_{298} = 14.088T + 4.878 \times 10^{-5}\,T^2 - 5548.7 \log T + 9522.88 . \quad (165)$$

A small correction term, negligible above 500°K, is omitted.

[382] Kelley, K.K., J. Am. Chem. Soc. 61, 1217 (1939).

[383] Nilson, L.F. and O. Pettersson, Ber. Chem. Gesell. 13, 1459 (1880).

c) Kandyba et al[375] (1200° to 2820°K in cal/gfw)

$$H_T^o - H_{298}^o = 9.471\,T + 1.045 \times 10^{-3}\,T^2 - 3540 . \qquad (166)$$

For the present compilation, the extrapolated heat capacity data of Victor and Douglas[78] were joined at 1500°K with the heat capacity data of Kandyba et al.[375] The result of this procedure was a heat content at 2800°K, 3.5 percent greater than that tabulated by the National Bureau of Standards[78] from an extrapolation of the data of Victor and Douglas.[78]

The uncertainty assigned to the heat content was one percent up to 1500°K, and was increased to two percent at the melting point.

The heat capacity of liquid BeO was assumed to be 17 cal/°K gfw. Thermodynamic functions of the condensed phases of BeO are given in Table LIV. Analyses of heat-of-formation data had not been completed at the time of report writing.

c. Thermodynamic Properties of Ideal Molecular Gas

The thermodynamic functions of BeO gas were calculated with the computer program based on the treatment of the diatomic molecule outlined in section III-E of this report. The spectroscopic constants used were those given by Herzberg.[54] All the electronic states listed in that reference were included in the calculation. The constants were converted to those for a naturally occurring isotopic mixture by the procedure discussed in section IV-A12 from data for the isotopic masses and abundances from the same sources. Values of D_e for some of the states were estimated from Dunham's[53] equations. The constants (in units of cm^{-1}) used were as follows:

Constant	$X^1\Sigma^+$	$A^1\Pi$	$B^1\Sigma^+$	$C(^1\Sigma)$	$D^1\Pi$
E	0	9234.93	211196.7	38917.9	41130
ω_e	1487.256	1144.187	1370.755	1081.4	1016
$\omega_e x_e$	11.8286	8.4137	7.7448	9.1	10
$\omega_e y_e$	0.02335	0.03389	-0.00027	0	0
B_e	1.6509	1.3660	1.5757	1.308	0
α_e	0.0190	0.01628	0.0154	0.01	0
$D_e (\times 10^6)$	8.198	7.78	8.3	7.6	0
γ_e	0	0	0	---	0
g	1	2	1	---	[illegible]

TABLE LIV

BERYLLIUM OXIDE — CONDENSED PHASES — BeO

gfw = 25.013 — m.p. = 2820° ± 15°K

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-0.687			Infinite
298.15	6.105	3.376	3.376	0.000			
300	6.148	3.414	3.376	0.011			
400	8.083	5.467	3.643	0.730			
500	9.310	7.412	4.204	1.604			
600	10.128	9.186	4.889	2.578			
700	10.714	10.793	5.619	3.622			
800	11.154	12.254	6.359	4.716			
900	11.498	13.588	7.089	5.849			
1000	11.776	14.815	7.801	7.014			
1100	12.005	15.948	8.491	8.203			
1200	12.197	17.001	9.157	9.413			
1300	12.361	17.984	9.798	10.641			
1400	12.503	18.905	10.416	11.885			
1500	12.628	19.772	11.011	13.142			
1556	12.723	20.235	11.333	13.851			
1556	12.723	20.235	11.333	13.851			
1600	12.815	20.592	11.584	14.412			
1700	13.024	21.375	12.137	15.704			
1800	13.233	22.125	12.671	17.017			
1900	13.442	22.846	13.188	18.351			
2000	13.651	23.541	13.688	19.706			
2100	13.860	24.212	14.174	21.081			
2200	14.069	24.862	14.645	22.478			
2300	14.278	25.492	15.103	23.895			
2400	14.487	26.104	15.549	25.333			
2500	14.696	26.699	15.982	26.792			
2600	14.905	27.280	16.406	28.272			
2700	15.114	27.846	16.819	29.774			
2754	15.227	28.146	17.037	30.593			
2754	15.227	28.146	17.037	30.593			
2800	15.323	28.400	17.223	31.295			
2820	15.365	28.509	17.303	31.602			
2820	17.000	33.984	17.303	47.042			
2900	17.000	34.459	17.769	48.402			
3000	17.000	35.036	18.335	50.102			
3100	17.000	35.593	18.883	51.802			
3200	17.000	36.133	19.414	53.502			
3300	17.000	36.656	19.928	55.202			
3400	17.000	37.164	20.428	56.902			
3500	17.000	37.656	20.913	58.602			
3600	17.000	38.135	21.384	60.302			
3700	17.000	38.601	21.844	62.002			
3800	17.000	39.054	22.290	63.702			
3900	17.000	39.496	22.726	65.402			
4000	17.000	39.926	23.150	67.102			
4100	17.000	40.346	23.565	68.802			
4200	17.000	40.756	23.970	70.502			

BERYLLIUM OXIDE CONDENSED PHASES

SUMMARY OF UNCERTAINTY ESTIMATES

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	± .100	± .050	± .050	± .000			
1000	± .300	± .150	± .080	± .070			
2000	± .700	± .290	± .150	± .270			
2820	±1.580	± .444	± .220	± .630			
2820	±1.000	± .620	± .220	±1.130			
4000	±2.000	±1.140	± .420	±2.900			

$H^{\circ}_{298} - H^{\circ}_{0}$ was calculated to be 2076.6 cal/gfw.

The results of all the calculations are given in Table LV. The National Bureau of Standards[78] has reported thermodynamic functions of gaseous BeO calculated from spectroscopic constants for the ground state alone.

No attempt has been made to give uncertainties for the above calculations at this time. The real uncertainty results from the effect of neglecting triplet states, which doubtless exist, but which have not been reported. Because BeO is isoelectronic with C_2, a similar sequence of states might be expected in the two gaseous molecules. Among other states, C_2 has a $^1\Sigma^+_g$ ground state, a $^3\Pi_u$ state only 610 cm^{-1} above the ground state, and a $^3\Sigma^-_g$ state 6243.5 cm^{-1} above the ground state.[162] It is intended that additional calculations for gaseous BeO will be made after reasonable estimates of additional states are obtained.

The analysis of the heat-of-formation data had not been completed at time of report writing, and ΔH°_f, ΔF°_f and $\log_{10} K_p$ could not be included.

TABLE LV

BERYLLIUM OXIDE — IDEAL MOLECULAR GAS — BeO

gfw = 25.013 m.p. = 2820° ± 15°K

T, °K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal/gfw)	ΔH_f° (Kcal/gfw)	ΔF_f° (Kcal/gfw)	Log K_p
0	0.000	0.000	Infinite	-2.077			Infinite
298.15	7.046	47.209	47.209	0.000			
300	7.049	47.252	47.209	0.013			
400	7.254	49.306	47.488	0.727			
500	7.510	50.952	48.021	1.465			
600	7.757	52.344	48.628	2.229			
700	7.970	53.556	49.248	3.016			
800	8.146	54.632	49.855	3.822			
900	8.289	55.600	50.440	4.644			
1000	8.406	56.480	51.001	5.479			
1100	8.504	57.285	51.536	6.324			
1200	8.588	58.029	52.046	7.179			
1300	8.665	58.720	52.534	8.042			
1400	8.737	59.364	52.999	8.912			
1500	8.810	59.970	53.443	9.789			
1556	8.852	60.290	53.681	10.284			
1556	8.852	60.290	53.681	10.284			
1600	8.885	60.541	53.869	10.674			
1700	8.966	61.082	54.278	11.567			
1800	9.052	61.597	54.670	12.467			
1900	9.146	62.088	55.048	13.377			
2000	9.246	62.560	55.412	14.297			
2100	9.353	63.014	55.763	15.227			
2200	9.465	63.451	56.103	16.167			
2300	9.582	63.875	56.431	17.120			
2400	9.703	64.285	56.750	18.084			
2500	9.827	64.684	57.060	19.061			
2600	9.951	65.072	57.360	20.049			
2700	10.076	65.450	57.653	21.051			
2754	10.142	65.649	57.807	21.598			
2754	10.142	65.649	57.807	21.598			
2800	10.199	65.818	57.938	22.065			
2820	10.223	65.890	57.994	22.270			
2820	10.223	65.890	57.994	22.270			
2900	10.320	66.179	58.216	23.091			
3000	10.437	66.530	58.488	24.128			
3100	10.551	66.875	58.753	25.178			
3200	10.659	67.212	59.012	26.239			
3300	10.763	67.541	59.266	27.310			
3400	10.861	67.864	59.514	28.391			
3500	10.953	68.181	59.757	29.482			
3600	11.038	68.491	59.996	30.582			
3700	11.118	68.794	60.229	31.690			
3800	11.191	69.092	60.459	32.806			
3900	11.258	69.384	60.684	33.929			
4000	11.319	69.670	60.906	35.058			
4100	11.374	69.950	61.123	36.193			
4200	11.423	70.226	61.337	37.333			
4300	11.467	70.495	61.547	38.478			
4400	11.506	70.760	61.754	39.628			
4500	11.540	71.019	61.957	40.780			
4600	11.570	71.274	62.157	41.937			
4700	11.595	71.523	62.354	43.096			
4800	11.617	71.768	62.548	44.257			
4900	11.635	72.008	62.739	45.421			
5000	11.649	72.244	62.927	46.586			
5100	11.661	72.476	63.113	47.752			
5200	11.669	72.703	63.295	48.920			
5300	11.676	72.926	63.475	50.088			
5400	11.680	73.145	63.653	51.257			
5500	11.682	73.360	63.828	52.427			
5600	11.682	73.572	64.001	53.597			
5700	11.681	73.779	64.171	54.766			
5800	11.678	73.983	64.339	55.936			
5900	11.674	74.184	64.505	57.105			
6000	11.670	74.381	64.669	58.274			

2. Calcium Oxide (CaO)

a. Crystal Structure and Melting Point

Calcium oxide has a face-centered cubic (NaCl type) structure at room temperature[57] which presumably persists up to the melting point. Beals and Cook[384] measured the lattice parameters up to 1500°K by X-ray methods.

Ol'shanskii[376] gave the melting point of CaO as 2893°K. Schumacher[385] reported it to be 2849°K, and Kanolt[386] gave a value of 2843°K. The average for these values of 2860° ± 30°K was adopted here.

b. Thermodynamic Properties of the Condensed Phases

1) Heat of fusion

The entropy of fusion of CaO was assumed to be 6.0 ± 0.5 cal/°K gfw, which corresponded to a heat of fusion of 17.2 ± 1.4 Kcal/°K gfw. Kubaschewski and Evans[182] estimated the latter quantity to be 19 Kcal/gfw. Kelley[137] used a heat-of-fusion value of 12.24 Kcal/° K gfw from melting points in the CaO-ZrO_2 system.

2) Entropy and heat content at 298.15°K

The low-temperature heat capacity of CaO was measured by Nernst and Schwers[233] (28° to 90°K) and by Parks and Kelley[387] (87° to 293°K). From these data, S^o_{298} was calculated to be 9.561 ± 0.15 cal/°K gfw, and $H^o_{298} - H^o_0$ was calculated to be 1668 cal/gfw.

3) High-temperature heat content

The heat content equation given by Kelley[56] in cal/gfw for use up to 2000°K was adopted here and extrapolated to the melting point.

$$H^o_T - H^o_{298} = 11.67T + 0.54 \times 10^{-3}T^2 + 1.56 \times 10^5T^{-1} - 4051 \quad . (167)$$

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[384] Beals, R. and R. Cook, J. Am. Ceram. Soc. 40, 279 (1957).

[385] Schumacher, E. E., J. Am. Chem. Soc. 48, 396 (1926).

[386] Kanolt, L., J. Wash. Acad. Sci. 3, 315 (1931).

[387] Parks, G. S. and K. K. Kelley, J. Phys. Chem. 30, 47 (1926).

The uncertainty assigned to the heat content up to 1000°K was 1 percent and this was increased to 2 percent at the melting point. Kelley's[56] equation was based primarily on the data of Lander[388] (298° to 1177°K).

The heat capacity of liquid CaO was assumed to be 16.5 cal/°K gfw. The calculated thermodynamic functions for the condensed phases of CaO are given in Table LVI. The analysis of the heat-of-formation data in the literature was not completed at the time of report writing. Uncertainity estimates are summarized on the back of the Table.

c. Thermodynamic Properties of the Gaseous Phase

The thermodynamic functions of gaseous, molecular calcium oxide were calculated with the computer program based on the treatment of the diatomic molecule outlined in section III-E of this report. The spectroscopic constants used (in units of cm^{-1}) were taken from Hultin and Lagerqvist,[389] and Lagerqvist.[390]

Constant	$X\ ^1\Sigma$	$A\ ^1\Sigma$	$B\ ^1\Pi$	$C\ ^1\Sigma$
E	0	11584.84	25913.0	28772.4
ω_e	732.11	716.0	580.0	560.9
$\omega_e x_e$	4.81	1.60	2.80	4.0
$\omega_e y_e$	---	---	---	---
B_e	0.44447	0.4063	0.3882	0.3731
α_e	0.00335	0.00141	0.0055	0.0032
γ_e	---	---	---	---
$D_e (\times 10^6)$	0.656	0.54	0.70	0.70
g	1	1	2	1

No corrections were made for the naturally occurring isotopic mixture.

388 Lander, J. J., J. Am. Chem. Soc. 73, 5794 (1951).

389 Hultin, M. and A. Lagerqvist, Ark. Fys. 2, 471 (1950).

390 Lagerqvist, A., Ark. Fys. 8, 83 (1954).

gfw = 56.08 m.p. = 2860° ± 30°K

T, °K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal/gfw)	ΔH_f° (Kcal/gfw)	ΔF_f° (Kcal/gfw)	Log K_p
0	0.000	0.000	Infinite	-1.668			Infinite
298.15	10.230	9.561	9.561	0.000			
300	10.254	9.624	9.561	0.019			
400	11.120	12.708	9.976	1.093			
500	11.579	15.243	10.783	2.230			
600	11.878	17.382	11.709	3.404			
700	12.101	19.231	12.655	4.603			
737	12.172	19.856	13.001	5.052			
737	12.172	19.856	13.001	5.052			
800	12.283	20.859	13.581	5.827			
900	12.442	22.315	14.472	7.059			
1000	12.587	23.634	15.324	8.310			
1100	12.722	24.840	16.135	9.576			
1123	12.752	25.103	16.315	9.869			
1123	12.752	25.103	16.315	9.869			
1200	12.851	25.952	16.906	10.855			
1300	12.975	26.986	17.643	12.146			
1400	13.095	27.952	18.345	13.450			
1500	13.214	28.859	19.016	14.765			
1600	13.330	29.716	19.658	16.092			
1700	13.445	30.527	20.273	17.431			
1765	13.519	31.033	20.661	18.307			
1765	13.519	31.033	20.661	18.307			
1800	13.559	31.299	20.865	18.781			
1900	13.672	32.035	21.433	20.143			
2000	13.784	32.739	21.981	21.516			
2100	13.896	33.414	22.509	22.900			
2200	14.007	34.063	23.020	24.295			
2300	14.117	34.688	23.514	25.701			
2400	14.228	35.292	23.993	27.118			
2500	14.338	35.875	24.457	28.546			
2600	14.448	36.439	24.906	29.986			
2700	14.365	36.986	25.343	31.436			
2800	14.667	37.518	25.769	32.897			
2860	14.733	37.830	26.019	33.779			
2860	16.500	43.844	26.019	50.979			
2900	16.500	44.073	26.266	51.639			
3000	16.500	44.632	26.869	53.289			
3100	16.500	45.173	27.451	54.939			
3200	16.500	45.697	28.013	56.589			
3300	16.500	46.205	28.557	58.239			
3400	16.500	46.698	29.084	59.889			
3500	16.500	47.176	29.593	61.539			
3600	16.500	47.640	30.088	63.189			
3700	16.500	48.093	30.569	64.839			
3800	16.500	48.533	31.036	66.489			
3900	16.500	48.961	31.489	68.139			
4000	16.500	49.379	31.932	69.789			

CALCIUM OXIDE CONDENSED PHASES

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	cal/°K gfw			Kcal/gfw			Log K_p
	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	
298.15	± .200	± .150	± .150	± .000			
1000	± .430	± .290	± .210	± .080			
2000	± .930	± .460	± .300	± .330			
2860	±1.740	± .610	± .370	± .680			
2860	±1.000	±1.100	± .370	±2.080			
4000	±2.000	±1.600	± .650	±3.790			

The thermodynamic functions of molecular CaO (gas) calculated with the above spectroscopic constants are given in Table LVII. It is not certain[391-393] that the ground state of CaO (g) is a singlet state. Therefore, uncertainties have not been determined for the present calculation pending further analysis of the effect of assuming other possible energy level schemes. Thermodynamic functions based on the assumption of the singlet ground state were also given by Kelley,[56] and Veits and Gurvich.[394] $H^\circ_{298} - H^\circ_0$ was found to be 2,140 cal/mole.

The review of data for the heat of formation of CaO(g) was not completed at the time of report writing, and ΔH°_f , ΔF°_f , and $\log_{10}K_p$ could not be included.

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[391] Brewer, L. and R. F. Porter, J. Chem. Phys. 22, 1867 (1954).

[392] Lagerqvist, A. and L. Huldt, Ark. Fys. 8, 427 (1954).

[393] Huldt, L. and A. Lagerqvist, Ark. Fys. 9, 227 (1955).

[394] Veits, I. and L. Gurvich, Zhur. Fiz. Khim. 32, 2532 (1958).

TABLE LVII

CALCIUM OXIDE | IDEAL MOLECULAR GAS | CaO

gfw = 56.08 m.p. = 2860° ± 30°K

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-2.140			Infinite
298.15	7.758	52.489	52.489	0.000			
300	7.766	52.537	52.489	0.014			
400	8.148	54.827	52.799	0.811			
500	8.399	56.674	53.395	1.640			
600	8.565	58.221	54.074	2.488			
700	8.679	59.551	54.764	3.351			
737	8.712	59.998	55.013	3.674			
737	8.712	59.998	55.013	3.674			
800	8.762	60.715	55.437	4.223			
900	8.825	61.751	56.082	5.103			
1000	8.874	62.684	56.696	5.988			
1100	8.914	63.531	57.280	6.877			
1123	8.922	63.713	57.407	7.082			
1123	8.922	63.713	57.407	7.082			
1200	8.948	64.309	57.833	7.770			
1300	8.978	65.026	58.359	8.666			
1400	9.005	65.692	58.860	9.566			
1500	9.030	66.315	59.336	10.467			
1600	9.055	66.898	59.791	11.372			
1700	9.079	67.448	60.226	12.278			
1765	9.096	67.787	60.496	12.869			
1765	9.096	67.787	60.496	12.869			
1800	9.105	67.968	60.642	13.187			
1900	9.131	68.461	61.040	14.099			
2000	9.159	68.930	61.423	15.014			
2100	9.189	69.378	61.792	15.931			
2200	9.220	69.807	62.147	16.851			
2300	9.254	70.217	62.489	17.775			
2400	9.289	70.612	62.820	18.702			
2500	9.326	70.993	63.139	19.633			
2600	9.365	71.360	63.449	20.567			
2700	9.406	71.714	63.749	21.506			
2800	9.449	72.058	64.040	22.449			
2860	9.475	72.258	64.210	23.017			
2860	9.475	72.258	64.210	23.017			
2900	9.492	72.391	64.323	23.396			
3000	9.537	72.714	64.598	24.347			
3100	9.583	73.028	64.866	25.303			
3200	9.630	73.334	65.126	26.264			
3300	9.678	73.631	65.380	27.229			
3400	9.726	73.922	65.628	28.199			
3500	9.775	74.205	65.870	29.174			
3600	9.825	74.482	66.106	30.154			
3700	9.874	74.753	66.337	31.139			
3800	9.925	75.018	66.563	32.129			
3900	9.976	75.278	66.785	33.123			
4000	10.027	75.532	67.001	34.123			
4100	10.078	75.782	67.214	35.128			
4200	10.130	76.026	67.422	36.138			
4300	10.183	76.267	67.626	37.154			
4400	10.235	76.503	67.827	38.174			
4500	10.289	76.735	68.024	39.200			
4600	10.343	76.963	68.218	40.231			
4700	10.397	77.188	68.408	41.268			
4800	10.452	77.409	68.595	42.309			
4900	10.507	77.627	68.779	43.357			
5000	10.564	77.842	68.960	44.410			
5100	10.620	78.054	69.138	45.468			
5200	10.678	78.263	69.314	46.532			
5300	10.736	78.469	69.487	47.602			
5400	10.795	78.672	69.658	48.678			
5500	10.854	78.873	69.826	49.760			
5600	10.915	79.072	69.992	50.848			
5700	10.976	79.268	70.156	51.941			
5800	11.037	79.462	70.317	53.041			
5900	11.100	79.654	70.477	54.147			
6000	11.163	79.844	70.634	55.260			

3. Chromium Oxides

The compilation of thermodynamic data for both condensed and gaseous phases of the chromium oxides was in progress at the time of report writing. The thermodynamic functions for gaseous chromium dioxide (CrO_2) and gaseous chromium trioxide (CrO_3) were included in this report; the remainder will be reported later.

a. Chromium Dioxide (CrO_2)

No experimental spectroscopic data had been reported for gaseous chromium dioxide. All of the molecular constants required in the calculation of the thermodynamic functions of CrO_2 were therefore estimated. The thermodynamic functions for gaseous CrO_2 given in Table LVIII were calculated by means of the computer program described in section III-F with the following molecular data:

Molecular configuration

Symmetric nonlinear molecule with

$$\angle O-Cr-O = 107 \text{ deg.}$$

$$r_o = 1.627 \text{ Å}$$

Product of moments of inertia

$$I_A I_B I_C = 340637 \times 10^{-120} g^3 cm^6$$

Symmetry number

$$\theta = 2 \quad .$$

Fundamental frequencies

$$\omega_1 = 870 \text{ cm}^{-1}$$

$$\omega_2 = 388 \text{ cm}^{-1}$$

$$\omega_3 = 926 \text{ cm}^{-1} \quad .$$

Ground electronic state

$$^1\Sigma \quad .$$

TABLE LVIII

CHROMIUM DIOXIDE — IDEAL MOLECULAR GAS — CrO_2

gfw = 84.01

T, °K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal/gfw)	ΔH_f° (Kcal/gfw)	ΔF_f° (Kcal/gfw)	Log K_p
0	0.000	0.000	Infinite	-2.640			Infinite
298.15	10.453	61.856	61.856	0.000			
300	10.473	61.921	61.856	0.019			
400	11.422	65.071	62.279	1.117			
500	12.085	67.696	63.107	2.294			
600	12.537	69.942	64.064	3.527			
700	12.849	71.899	65.046	4.797			
800	13.070	73.630	66.013	6.093			
900	13.230	75.179	66.947	7.409			
1000	13.350	76.580	67.842	8.738			
1100	13.441	77.857	68.695	10.078			
1200	13.512	79.029	69.508	11.426			
1300	13.569	80.113	70.282	12.780			
1400	13.614	81.120	71.021	14.139			
1500	13.651	82.061	71.726	15.502			
1600	13.681	82.943	72.400	16.869			
1700	13.707	83.773	73.045	18.239			
1800	13.728	84.557	73.663	19.610			
1900	13.747	85.300	74.256	20.984			
2000	13.762	86.006	74.826	22.360			
2100	13.776	86.677	75.374	23.737			
2200	13.788	87.319	75.903	25.115			
2300	13.798	87.932	76.413	26.494			
2400	13.807	88.519	76.905	27.874			
2500	13.815	89.083	77.381	29.256			
2600	13.822	89.625	77.841	30.637			
2700	13.829	90.147	78.288	32.020			
2800	13.834	90.650	78.720	33.403			
2900	13.840	91.135	79.140	34.787			
3000	13.844	91.605	79.548	36.171			
3100	13.848	92.059	79.944	37.556			
3200	13.852	92.498	80.329	38.941			
3300	13.856	92.925	80.705	40.326			
3400	13.859	93.338	81.070	41.712			
3500	13.862	93.740	81.426	43.098			
3600	13.864	94.131	81.774	44.484			
3700	13.867	94.511	82.113	45.871			
3800	13.869	94.880	82.444	47.258			
3900	13.871	95.241	82.768	48.645			
4000	13.873	95.592	83.084	50.032			
4100	13.875	95.934	83.393	51.419			
4200	13.877	96.269	83.696	52.807			
4300	13.878	96.595	83.992	54.195			
4400	13.880	96.914	84.282	55.582			
4500	13.881	97.226	84.566	56.970			
4600	13.882	97.532	84.845	58.359			
4700	13.884	97.830	85.118	59.747			
4800	13.885	98.122	85.386	61.135			
4900	13.886	98.409	85.649	62.524			
5000	13.887	98.689	85.907	63.912			
5100	13.888	98.964	86.160	65.301			
5200	13.889	99.234	86.409	66.690			
5300	13.889	99.498	86.653	68.079			
5400	13.890	99.758	86.894	69.468			
5500	13.891	100.013	87.130	70.857			
5600	13.892	100.263	87.362	72.246			
5700	13.892	100.509	87.591	73.635			
5800	13.893	100.751	87.816	75.024			
5900	13.893	100.988	88.037	76.414			
6000	13.894	101.222	88.255	77.803			

1) Molecular configuration

The molecular configuration of CrO_2 was unknown. Consideration of the periodic group to which chromium belongs and the work of Walsh[395] on bonding and structural relations led to the conclusion that CrO_2 was a symmetric, nonlinear molecule. Therefore, it was so considered in the present work. In the absence of experimental evidence, it is to be expected that some other workers would accept the alternative conclusion that it is linear symmetric. For example, the free-energy function of CrO_2 at several selected temperatures was recently calculated by Grimley, Burns, and Inghram[396] on the assumption of Chandrasekharaiah and Brewer[397] that the Group IV, V, and VI transition metal dioxides all form linear symmetric molecules. An O - Cr - O angle of 107 degrees was chosen in the present work as representing a reasonable value in comparison to known compounds of similar bonding. The Cr - O bond distance was assumed to be identical with the known corresponding distance for the chromium monoxide (CrO) molecule; i. e., 1.627Å.[398]

2) Moments of inertia

The moments of inertia of CrO_2 were calculated from the above bond angles and bond distances by means of equations[399] (168), (169), (170), and (171).

$$I_x = \left(\frac{2M_o M_{Cr}}{2M_o + M_{Cr}}\right) r_o^2 \cos^2\left(\frac{\zeta}{2}\right) \tag{168}$$

$$I_y = 2M_o r_o^2 \sin^2\left(\frac{\zeta}{2}\right) \tag{169}$$

$$I_z = I_x + I_y \tag{170}$$

$$I_A I_B I_C = I_x I_y I_z \quad . \tag{171}$$

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[395] Walsh, A. D., J. Chem. Soc. 2266 (1953).

[396] Grimley, R. T., R. P. Burns and M. G. Inghram, J. Chem. Phys. 34, 664 (1961).

[397] Chandrasekharaiah, M. S. and L. Brewer, U.S. AEC Rept UCRL-8736 (April 1959).

[398] Ninomiya, M., J. Phys. Soc. (Japan) 10, 829 (1955).

[399] Moelwyn-Hughes, E. A., Physical Chemistry, Pergamon Press, London (1957).

where

M_o = mass of oxygen atom

M_{Cr} = mass of chromium atom

and r_o = Cr - O bond distance

ζ = O - Cr - O bond angle.

3) Fundamental frequencies

The estimation of the fundamental frequencies of CrO_2 was based on the following three assumptions:

a) The fundamental vibrations may be described by a valence force-field method.[400]

b) The stretching force constant (k_1) for CrO_2 is the same as that for CrO. This assumption has been employed by previous workers.[396, 397] The stretching force constant for CrO was calculated from experimental spectroscopic data[398, 401] by means of equation (172).

$$k_1 = 4\pi^2 c^2 \mu \omega^2 \quad , \tag{172}$$

where

k_1 = stretching force constant

c = velocity of light

μ = reduced mass of CrO molecule

and

ω = vibrational frequency.

c) The ratio of the bond-bending and bond-stretching force constants is 0.0940, the average of those observed for several nonlinear molecules.[400]

$$k_\delta / k_1 \ell^2 = 0.0940. \tag{173}$$

400 Herzberg, G., Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand, N.Y. (1945).

401 Brewer, L. and M. S. Chandrasekharaiah, U.S. AEC Rept. UCRL-8717 Rev. (June 1960).

The values of the fundamental frequencies (ω_1, ω_2, and ω_3) were therefore calculated from equations (174), (175), and (176).

$$\omega_3^2 = \frac{\left[1 + \frac{2M_o}{M_{Cr}} \sin^2 \alpha\right] \frac{k_1}{M_o}}{0.3548 \times 10^{23}} \qquad (174)$$

$$\omega_1^2 + \omega_2^2 = \frac{\left[1 + \frac{2M_o}{M_{Cr}} \cos^2 \alpha\right] \frac{k_1}{M_o} + \frac{2}{M_o}\left[1 + \frac{2M_o}{M_{Cr}} \sin^2 \alpha\right] \frac{k_\delta}{\ell^2}}{0.3548 \times 10^{23}} \qquad (175)$$

$$\omega_1^2 \, \omega_2^2 = \frac{2\left[1 + \frac{2M_o}{M_{Cr}}\right] \frac{k_1}{M_o^2} \frac{k_\delta}{\ell^2}}{0.1259 \times 10^{46}}, \qquad (176)$$

where

$$\alpha = \frac{\zeta}{2} \qquad (177)$$

4) Electronic states

The electronic states of CrO_2 were unknown. The general practice, when no data are available, of considering only the ground state and assuming it to be a $^1\Sigma$ state has been followed in this work. This procedure is simpler and is believed to be as correct as that used by other workers[397, 401] who have estimated electronic levels from a crude ionic central atom model.

It should be emphasized that the thermodynamic functions of gaseous CrO_2 in Table LVIII represent "reasonable" estimates only; the numerical values could be appreciably altered should experimentally determined molecular constants become available for CrO_2 . $H^\circ_{298} - H^\circ_0$ was found to be 2,640 cal/mole.

b. Chromium Trioxide (CrO_3)

Experimental spectroscopic data also had not been reported for gaseous chromium trioxide. All of the molecular constants required in the calculation of the thermodynamic functions of CrO_3 were again estimated. The thermodynamic functions for gaseous CrO_3 given in Table LIX were also calculated by means of the machine program described in section III-F with the following molecular data:

Molecular configuration

Planar, symmetrical, cart-wheel molecule with

$\angle O-Cr-O = 120$ deg.

$r_0 = 1.627 \text{Å}$

TABLE LIX

CHROMIUM TRIOXIDE — IDEAL MOLECULAR GAS — CrO_3

gfw = 100.01

T, °K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal/gfw)	ΔH_f° (Kcal/gfw)	ΔF_f° (Kcal/gfw)	Log K_p
0	0.000	0.000	Infinite	-3.108			Infinite
298.15	13.881	64.500	64.500	0.000			
300	13.916	64.586	64.500	0.026			
400	15.533	68.824	65.067	1.503			
500	16.663	72.419	66.187	3.116			
600	17.441	75.530	67.491	4.824			
700	17.984	78.262	68.839	6.596			
800	18.371	80.690	70.171	8.415			
900	18.654	82.871	71.463	10.267			
1000	18.867	84.848	72.704	12.144			
1100	19.029	86.654	73.892	14.039			
1200	19.156	88.316	75.025	15.948			
1300	19.257	89.853	76.108	17.869			
1400	19.338	91.283	77.141	19.799			
1500	19.404	92.620	78.129	21.736			
1600	19.459	93.874	79.074	23.679			
1700	19.505	95.055	79.980	25.628			
1800	19.543	96.171	80.849	27.580			
1900	19.576	97.229	81.683	29.536			
2000	19.605	98.233	82.486	31.495			
2100	19.629	99.191	83.259	33.457			
2200	19.650	100.104	84.004	35.421			
2300	19.669	100.978	84.723	37.387			
2400	19.685	101.816	85.418	39.355			
2500	19.700	102.619	86.090	41.324			
2600	19.713	103.392	86.741	43.295			
2700	19.724	104.137	87.371	45.266			
2800	19.734	104.854	87.983	47.239			
2900	19.744	105.547	88.577	49.213			
3000	19.752	106.216	89.154	51.188			
3100	19.760	106.864	89.714	53.164			
3200	19.766	107.491	90.260	55.140			
3300	19.773	108.100	90.792	57.117			
3400	19.779	108.690	91.309	59.094			
3500	19.784	109.264	91.814	61.073			
3600	19.789	109.821	92.307	63.051			
3700	19.793	110.363	92.787	65.030			
3800	19.797	110.891	93.257	67.010			
3900	19.801	111.405	93.716	68.990			
4000	19.804	111.907	94.164	70.970			
4100	19.808	112.396	94.603	72.951			
4200	19.811	112.873	95.032	74.931			
4300	19.814	113.339	95.453	76.913			
4400	19.816	113.795	95.864	78.894			
4500	19.819	114.240	96.268	80.876			
4600	19.821	114.676	96.663	82.858			
4700	19.823	115.102	97.051	84.840			
4800	19.825	115.520	97.431	86.823			
4900	19.827	115.928	97.805	88.805			
5000	19.829	116.329	98.171	90.788			
5100	19.831	116.722	98.531	92.771			
5200	19.832	117.107	98.885	94.754			
5300	19.834	117.484	99.232	96.737			
5400	19.835	117.855	99.574	98.721			
5500	19.836	118.219	99.909	100.704			
5600	19.838	118.577	100.239	102.688			
5700	19.839	118.928	100.564	104.672			
5800	19.840	119.273	100.884	106.656			
5900	19.841	119.612	101.198	108.640			
6000	19.842	119.945	101.508	110.624			

Product of moments of inertia

$$I_A I_B I_C = 2346881 \times 10^{-120} g^3 cm^6$$

Symmetry number

$$\theta = 6 \quad .$$

Fundamental frequencies

$$\omega_1 = 840 \text{ cm}^{-1}$$

$$\omega_2 = 397 \text{ cm}^{-1}$$

$$\omega_3 = 1023 \text{ cm}^{-1}(2)$$

$$\omega_4 = 347 \text{ cm}^{-1}(2)$$

Ground electronic state

$$^1\Sigma$$

1) Molecular configuration

The molecular configuration of CrO_3 was unknown. The molecule was assumed to be of the symmetrical, planar, cart-wheel type. The only resonable alternative structure was pyramidal, but the pyramidal structure was considered to be unlikely in view of the known planar structure of other molecules having central atoms in the same periodic group as chromium; e.g., SO_3. The Cr - O bond distance was also assumed in this case to be identical with the known distance for the chromium monoxide (CrO) molecule; i.e., 1.627Å.[398]

2) Moments of inertia

The moments of inertia of CrO_3 were calculated for the assumed structure by means of equations[399] (170), (171), and (178).

$$I_{xx} = I_y = \frac{3M_o r_o^2}{2} , \tag{178}$$

where the symbols are as defined in section IV-B3a above.

3) Fundamental frequencies

The estimation of the fundamental frequencies of CrO_3 was based on the following assumptions:

a) Assumption (a) in paragraph a(3) above for CrO_2.

b) The stretching force constant (k_1) for CrO_3 may be calculated from an estimated value for the corresponding frequency ω_1 according to equation (179).

$$k_1 = 0.3548 \times 10^{23} M_o \, \omega_1^2 \quad . \tag{179}$$

The value of ω_1 was estimated on the assumption that the CrO_3 molecule could be considered approximately a CrO_2 molecule ($\angle O\text{-}Cr\text{-}O = 120°$) with an additional O atom attached. A value of ω_1^* corresponding to this pseudo-molecule was then calculated by the procedure described in the preceding section on the CrO_2 molecule.

The value 847 cm^{-1} was thus obtained for ω_1^*. It was then arbitrarily lowered to take into account the additional mass of the third oxygen atom. The final value for ω_1 was 840 cm^{-1}.

c) The other force constants (k_Δ and k_δ) may be evaluated by averaging the ratios of force constants calculated from observed frequencies for several planar, symmetrical, cartwheel molecules.[400] These averages for CrO_3 were

$$k_\delta / k_1 \ell^2 = 0.0440 \quad , \tag{180}$$

$$k_\Delta / k_1 \ell^2 = 0.1160. \tag{181}$$

The values of the fundamental frequencies were then calculated from equations (182), (183), (184), and (185).

$$\omega_1^2 = \frac{k_1}{0.3548 \times 10^{23} M_o} \tag{182}$$

$$\omega_2^2 = \frac{\left[1 + \frac{3M_o}{M_{Cr}}\right]\left(\frac{1}{M_o}\right)\left(\frac{k_\Delta}{\ell^2}\right)}{0.3548 \times 10^{23}} \tag{183}$$

$$\omega_3^2 + \omega_4^2 = \frac{\left[1 + \frac{3M_o}{2M_{Cr}}\right]\left[\frac{k_1}{M_o} + \frac{3k_\delta}{M_o\,\ell^2}\right]}{0.3548 \times 10^{23}} \tag{184}$$

$$\omega_3^2\ \omega_4^2 = \frac{3\left[1 + \frac{3M_o}{M_{Cr}}\right]\left(\frac{k_1}{M_o}\right)\left(\frac{k_\delta}{\ell^2}\right)}{0.1259 \times 10^{46}} \tag{185}$$

4) Electronic states

The electronic states of CrO_3 were unknown. The general practice, when no data are available, of considering only the ground state and assuming it to be a $^1\Sigma$ state was also followed herein.

It should be emphasized here also that the thermodynamic functions for CrO_3 in Table LIX represent "reasonable" estimates only, and that the numerical values may be appreciably altered should experimental molecular constants become available for CrO_3. $H^o_{298} - H^o_0$ was found to be 3, 108 cal/mole.

4. Magnesium Oxide (MgO)

a. Crystal Structure and Melting Point

Crystalline magnesium oxide has a face-centered cubic (NaCl type) structure at room temperature,[57] which was assumed to persist up to the melting point. Engberg and Zehms[378] found the coefficient of expansion to be practically constant from 1300° to 2300°K. The melting point of MgO has been given as 2913°K by Ebert and Cohn[402] from phase studies in the $MgO-ZrO_2$ system. However, it has been almost universally accepted as 3075°K. This latter value was given by Kanolt,[386] Ruff and Schmidt,[403] and Wartenberg, Reusch, and Saran,[380] and was adopted here. An uncertainty of ± 50°K was assigned to it.

b. Thermodynamic Properties of Condensed Phases

1) Heat of fusion

The heat of fusion of MgO was calculated by Kelley[137] to be 18.5 Kcal/gfw from melting-point measurements in the $MgO-ZrO_2$ system. This value, which gave a reasonable value of 6.0 cal/°K gfw for the entropy of fusion, was adopted and assigned an uncertainty of 1.5 Kcal/gfw.

2) Entropy and heat content at 298.15°K

The low-temperature heat capacity of MgO has been measured by Gunther[143] (21° to 84°K), Parks and Kelley[387] (94° to 291°K), Giauque and Archibald[404] (20° to 301°K), Barron, Berg, and Morrison[405] (10° to 270°K), and Lien and Philips[406] (1.5 to 4°K). The data of Giauque and Archibald,[404] and Lien and Philips,[406] were from microcrystalline samples, and those of the other authors were from macrocrystalline samples. Results for these two crystalline states of MgO differed appreciably. For purposes of this compilation, the macrocrystalline state was taken as the standard state and data for it alone were tabulated.

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[402] Ebert, F. and E. Cohn, Z. anorg. Chem. 213, 321 (1933).

[403] Ruff, O. and P. Schmidt, Z. anorg. Chem. 117, 172 (1921).

[404] Giauque, W.F. and R.C. Archibald, J. Am. Chem. Soc. 59, 561 (1937).

[405] Barron, T.H.K., W.T. Berg, and J.A. Morrison, Proc. Roy. Soc. (London) 250A, 70 (1959).

[406] Lien, W. and N. Phillips, J. Chem. Phys. 29, 1415 (1958).

TABLE LX

MAGNESIUM OXIDE — CONDENSED PHASES — MgO

gfw = 40.32 m.p. = 3075° ± 50°K

T, °K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal/gfw)	ΔH_f° (Kcal/gfw)	ΔF_f° (Kcal/gfw)	Log K_p
0	0.000	0.000	Infinite	-1.235			Infinite
298.15	8.906	6.439	6.439	0.000			
300	8.939	6.495	6.440	0.017			
400	10.148	9.252	6.807	0.978			
500	10.854	11.599	7.538	2.031			
600	11.323	13.622	8.387	3.141			
700	11.656	15.393	9.263	4.291			
800	11.905	16.967	10.130	5.469			
900	12.098	18.381	10.970	6.670			
923	12.135	18.683	11.154	6.949			
923	12.135	18.683	11.154	6.949			
1000	12.251	19.663	11.775	7.888			
1100	12.375	20.837	12.547	9.119			
1200	12.478	21.918	13.283	10.362			
1300	12.565	22.921	13.987	11.614			
1377	12.622	23.644	14.505	12.584			
1377	12.622	23.644	14.505	12.584			
1400	12.638	23.855	14.659	12.874			
1500	12.701	24.729	15.301	14.141			
1600	12.756	25.550	15.916	15.414			
1700	12.804	26.325	16.506	16.692			
1800	12.845	27.058	17.072	17.975			
1900	12.882	27.754	17.616	19.261			
2000	12.915	28.415	18.139	20.551			
2100	12.945	29.046	18.644	21.844			
2200	12.971	29.649	19.131	23.140			
2300	12.994	30.226	19.601	24.438			
2400	13.016	30.780	20.055	25.739			
2500	13.035	31.311	20.494	27.042			
2600	13.052	31.823	20.921	28.346			
2700	13.068	32.316	21.334	29.652			
2800	13.082	32.791	21.734	30.959			
2900	13.095	33.251	22.124	32.268			
3000	13.107	33.695	22.502	33.578			
3075	13.115	34.019	22.779	34.562			
3075	14.600	40.035	22.779	53.062			
3100	14.600	40.153	22.918	53.427			
3200	14.600	40.617	23.465	54.887			
3300	14.600	41.066	23.991	56.347			
3400	14.600	41.502	24.500	57.807			
3500	14.600	41.925	24.992	59.267			
3600	14.600	42.336	25.467	60.727			
3700	14.600	42.736	25.929	62.187			
3800	14.600	43.125	26.376	63.647			
3900	14.600	43.505	26.811	65.107			
4000	14.600	43.875	27.233	66.567			

MAGNESIUM OXIDE CONDENSED PHASES

SUMMARY OF UNCERTAINTY ESTIMATES

T, °K	cal/°K gfw			Kcal/gfw			Log K_p
	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	
298.15	± .050	± .020	±.020	± .000			
1000	± .280	± .160	±.080	± .080			
2000	± .940	± .390	±.180	± .410			
3075	±1.780	± .570	±.290	± .860			
3075	±1.000	±1.060	±.290	±2.360			
4000	±2.000	±1.450	±.510	±3.750			

The National Bureau of Standards[78] joined the low-temperature data for the macroscopic solid phase with the unpublished data of Victor and Douglas (273° to 1173°K). The results of this analysis, which were accepted here, yielded a value for S°_{298} of 6.439 ± 0.020 cal/°K gfw and for $H^\circ_{298} - H^\circ_0$ of 1234.6 cal/gfw. Kelley[139] reported S°_{298} to be 6.4 ± 0.1 cal/°K gfw for macrocrystalline MgO.

3) High-temperature heat content

Results of the analysis of the unpublished data of Victor and Douglas by the National Bureau of Standards[78] was adopted for the high-temperature heat content of MgO. According to this analysis, the heat capacity of MgO from 450° to 1200°K in cal/°K gfw was given by equation (186).

$$C^\circ_p = 13.7146 - 4.494 \times 10^{-5} T - 1418/T \ . \tag{186}$$

The NBS report also stated that the enthalpies derived from this equation could be extrapolated from 1200° to 2100°K with an uncertainty of ± 2 percent. This uncertainty was presumably arrived at by comparison with Kelley's[56] tabulation. Kelley[56] derived equation (187) for the enthalpy in cal/gfw,

$$H^\circ_T - H^\circ_{298} = 10.18T + 0.87 \times 10^{-3} T^2 + 1.48 \times 10^5/T - 3609 \ . \tag{187}$$

from the data of Magnus[407] (288° to 1040°K) and Wilkes[408] (303° to 2073°K). The enthalpies tabulated by the NBS are from 1 to 5 percent higher than those given by Kelley,[56] with the maximum difference in the range from 700° to 800°K.

The heat capacity of liquid MgO was assumed to be 14.6 cal/°K gfw.

Thermodynamic functions of the condensed phases of MgO are given in Table LX. Analyses of heat-of-formation data had not been completed at the time of report writing. Uncertainly estimates are summarized on the back of the table.

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407 Magnus, A., Phys. Z. 14, 5 (1913).

408 Wilkes, G.B., J. Am. Ceram. Soc. 15, 72 (1932).

c. Thermodynamic Properties of the Ideal Molecular Gas

The thermodynamic functions of MgO gas were calculated with the computer program based on the treatment of the diatomic molecule outlined in section III-E of this report. The spectroscopic constants for the assumed $^1\Sigma$ ground state given by the National Bureau of Standards[78] were used. These constants had been corrected to those appropriate for the naturally occurring isotopic mixture. Spectroscopic constants for the $A\,^1\Pi$ and $B\,^1\Sigma$ states were taken from Herzberg.[54] Values of D_e for the excited states were estimated from Dunham's equations.[53, 54] Other electronic states of higher energy were listed by Herzberg,[54] but their positions with respect to the assumed ground state were not known. The constants used (in units of cm^{-1}) were as follows:

Constant	$X'^1\Sigma$	$A^1\Pi$	$B^1\Sigma$
E	0	3494.4	20004.7
ω_e	782.84	664.4	824.1
$\omega_e x_e$	5.15	3.91	4.76
$\omega_e y_e$	---	---	---
B_e	0.5711	0.5056	0.5822
α_e	0.005	0.0046	0.0045
γ_e	---	---	---
D_e $(\times 10^6)$	1.22	1.2	1.2
g	1	2	1

$H^{\circ}_{298} - H^{\circ}_{0}$ was calculated to be 2129.2 cal/gfw.

The results of all the computations are given in Table LXI. The National Bureau of Standards[78] has reported thermodynamic functions for gaseous MgO from spectroscopic constants for the ground state alone. Veits and Gurvich[394] used essentially the same constants as those adopted here to calculate thermodynamic functions up to 3500°K.

The calculations leading to Table LXI are subject to the same uncertainties as encountered with similar calculations discussed previously for BeO and CaO in sections IV - B1 and IV - B2, respectively, of this report. It is not certain that the lowest state of the observed singlet systems is the ground state. If one were to adopt the energy level diagram of MgO(g) given by Brewer and Porter[391] in which the ground state was postulated to be the $^3\Sigma$ state (with an adjacent $^3\Pi$ state) and to make reasonable estimates of spectroscopic constants of the triplet states, the free-energy functions at 298.15° and 6000°K would change from 50.960 and 70.453 cal/°K gfw, respectively (as tabulated in Table LXI), to 55.143 and 73.060 cal/°K gfw, respectively. However, the interpretation of the ultraviolet bands on which Brewer and Porter's[391] energy-level diagram was based is itself not certain as those bands may have been due to MgOH or a polyatomic oxide.[409] Analysis of the above uncertainties will therefore be a continuing activity.

The analysis of the heat-of-formation data of MgO(g) had not been completed at the time of report writing.

[409] Pesic, D. and A. Gaydon, Proc. Phys. Soc. (London) 73A, 244 (1959).

TABLE LXI

MAGNESIUM OXIDE — IDEAL MOLECULAR GAS — MgO

gfw = 40.32 — m.p. = 3075° $\pm$ 50°K

	cal/°K gfw				Kcal/gfw		
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-2.129			Infinite
298.15	7.668	50.960	50.960	0.000			
300	7.676	51.007	50.960	0.014			
400	8.069	53.272	51.266	0.803			
500	8.354	55.105	51.856	1.624			
600	8.591	56.649	52.530	2.472			
700	8.831	57.991	53.216	3.343			
800	9.093	59.187	53.889	4.239			
900	9.376	60.274	54.539	5.162			
923	9.445	60.513	54.683	5.381			
923	9.445	60.513	54.683	5.381			
1000	9.665	61.27[illegible]	55.163	6.114			
1100	9.945	62.212	55.762	7.095			
1200	10.201	63.088	56.336	8.102			
1300	10.423	63.914	56.888	9.134			
1377	10.565	64.517	57.296	9.944			
1377	10.565	64.517	57.296	9.944			
1400	10.606	64.693	57.418	10.186			
1500	10.749	65.430	57.928	11.254			
1600	10.854	66.128	58.419	12.334			
1700	10.925	66.788	58.892	13.423			
1800	10.968	67.414	59.348	14.518			
1900	10.986	68.008	59.789	15.616			
2000	10.984	68.572	60.214	16.715			
2100	10.968	69.108	60.625	17.813			
2200	10.941	69.618	61.023	18.909			
2300	10.906	70.104	61.407	20.001			
2400	10.865	70.567	61.780	21.090			
2500	10.821	71.010	62.141	22.174			
2600	10.776	71.435	62.490	23.255			
2700	10.730	71.841	62.830	24.330			
2800	10.685	72.231	63.159	25.401			
2900	10.642	72.606	63.479	26.468			
3000	10.601	72.967	63.790	27.530			
3075	10.572	73.228	64.017	28.324			
3075	10.572	73.228	64.017	28.324			
3100	10.562	73.315	64.093	28.589			
3200	10.525	73.651	64.387	29.644			
3300	10.492	73.975	64.673	30.695			
3400	10.461	74.289	64.953	31.743			
3500	10.433	74.593	65.225	32.789			
3600	10.407	74.888	65.490	33.831			
3700	10.385	75.174	65.749	34.872			
3800	10.365	75.452	66.002	35.910			
3900	10.348	75.723	66.249	36.946			
4000	10.333	75.986	66.491	37.981			
4100	10.320	76.243	66.727	39.015			
4200	10.310	76.493	66.958	40.047			
4300	10.302	76.738	67.185	41.079			
4400	10.295	76.977	67.406	42.110			
4500	10.291	77.210	67.624	43.140			
4600	10.288	77.439	67.837	44.170			
4700	10.287	77.662	68.045	45.200			
4800	10.288	77.882	68.250	46.230			
4900	10.290	78.096	68.451	47.261			
5000	10.293	78.307	68.649	48.291			
5100	10.298	78.514	68.843	49.322			
5200	10.304	78.717	69.034	50.354			
5300	10.311	78.917	69.221	51.386			
5400	10.319	79.113	69.405	52.419			
5500	10.328	79.306	69.587	53.453			
5600	10.338	79.495	69.765	54.488			
5700	10.349	79.682	69.941	55.525			
5800	10.360	79.866	70.114	56.562			
5900	10.372	80.047	70.285	57.600			
6000	10.385	80.226	70.453	58.640			

5. Molybdenum Oxides

The important oxides of molybdenum for which thermodynamic properties were available are molybdenum monoxide (MoO), molybdenum dioxide (MoO_2) and molybdenum trioxide (MoO_3). Although polymeric species of MoO_3; i. e., $(MoO_3)_2$, $(MoO_3)_3$, etc., are known to exist, there were insufficient basic data to permit the calculation of thermodynamic tables for them.

a. Molybdenum Monoxide (MoO)

Molybdenum monoxide does not appear to exist in the condensed phase,[264] but its existence in the vapor phase at high temperatures has been verified by mass spectrographic work.[410] Consequently, only the thermodynamic functions for gaseous MoO in Table LXII were prepared for the present compilation.

These thermodynamic functions were calculated by means of the computer program described in section III-F with the following estimated molecular data:

Bond distance

$$r_o = 1.73\ \text{Å}\ .$$

Moment of inertia

$$I = 68.139 \times 10^{-40} g\ cm^2\ .$$

Symmetry number

$$\theta = 1\ .$$

Fundamental frequency

$$\omega = 840\ cm^{-1}\ .$$

Ground electronic state

$$^1\Sigma$$

1) Bond distance

The Mo-O bond distance had not been experimentally determined. A value of 1.66 Å has been calculated[410] by means of the

[410] DeMaria, G., R. Burns, J. Drowart, and M. Inghram, J. Chem. Phys. 32, 1373 (1960).

TABLE LXII

MOLYBDENUM MONOXIDE — IDEAL MOLECULAR GAS — MoO

Reference State for Calculating ΔH_f°, ΔF_f°, and Log K_p : Solid Mo from 298.15° to 2890°K, Liquid Mo from 2890° to 4965° K, Gaseous Mo from 4965° to 6000° K; Gaseous O_2; Gaseous MoO.

gfw = 111.95

T, °K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal/gfw)	ΔH_f° (Kcal/gfw)	ΔF_f° (Kcal/gfw)	Log K_p
0	0.000	0.000	Infinite	-2.116	87.413	87.413	Infinite
298.15	7.542	54.587	54.587	0.000	87.400	80.467	-58.981
300	7.550	54.634	54.587	0.014	87.396	80.424	-58.586
400	7.932	56.861	54.888	0.789	87.232	78.124	-42.683
500	8.203	58.662	55.469	1.597	87.067	75.869	-33.161
600	8.388	60.175	56.130	2.427	86.897	73.643	-26.823
700	8.515	61.478	56.803	3.272	86.718	71.448	-22.306
800	8.604	62.621	57.461	4.129	86.537	69.278	-18.925
900	8.669	63.639	58.092	4.992	86.342	67.133	-16.301
1000	8.717	64.555	58.693	5.862	86.138	65.010	-14.207
1100	8.754	65.387	59.264	6.735	85.912	62.906	-12.498
1200	8.783	66.150	59.807	7.612	85.665	60.827	-11.078
1300	8.806	66.854	60.322	8.492	85.396	58.767	-9.879
1400	8.824	67.508	60.812	9.373	85.105	56.729	-8.855
1500	8.839	68.117	61.279	10.256	84.804	54.714	-7.971
1600	8.851	68.689	61.725	11.141	84.470	52.717	-7.200
1700	8.861	69.225	62.150	12.027	84.108	50.743	-6.523
1800	8.870	69.731	62.557	12.913	83.715	48.794	-5.924
1900	8.877	70.211	62.948	13.800	83.291	46.862	-5.390
2000	8.883	70.667	63.322	14.688	82.834	44.958	-4.913
2100	8.889	71.100	63.683	15.577	82.342	43.073	-4.482
2200	8.893	71.514	64.029	16.466	81.813	41.219	-4.095
2300	8.898	71.909	64.363	17.356	81.246	39.385	-3.742
2400	8.901	72.288	64.686	18.246	80.637	37.579	-3.422
2500	8.904	72.651	64.997	19.136	79.985	35.800	-3.129
2600	8.907	73.001	65.298	20.027	79.290	34.047	-2.862
2700	8.910	73.337	65.590	20.917	78.549	32.314	-2.615
2800	8.912	73.661	65.872	21.809	77.761	30.621	-2.390
2890	8.914	73.943	66.119	22.611	77.009	29.117	-2.202
2890	8.914	73.943	66.119	22.611	70.359	29.117	-2.202
2900	8.914	73.974	66.146	22.700	70.300	28.980	-2.184
3000	8.916	74.276	66.412	23.591	69.715	27.564	-2.008
3100	8.918	74.568	66.671	24.483	69.129	26.167	-1.845
3200	8.919	74.852	66.922	25.375	68.540	24.790	-1.693
3300	8.921	75.126	67.166	26.267	67.949	23.433	-1.552
3400	8.922	75.392	67.404	27.159	67.357	22.093	-1.420
3500	8.923	75.651	67.636	28.051	66.761	20.766	-1.297
3600	8.924	75.902	67.862	28.944	66.165	19.465	-1.182
3700	8.925	76.147	68.083	29.836	65.567	18.178	-1.074
3800	8.926	76.385	68.298	30.729	64.967	16.906	-0.972
3900	8.927	76.617	68.509	31.621	64.365	15.639	-0.876
4000	8.928	76.843	68.714	32.514	63.762	14.408	-0.787
4100	8.928	77.063	68.915	33.407	63.157	13.177	-0.702
4200	8.929	77.278	69.112	34.300	62.550	11.966	-0.623
4300	8.930	77.489	69.304	35.193	61.941	10.776	-0.548
4400	8.930	77.694	69.493	36.086	61.330	9.583	-0.476
4500	8.931	77.895	69.677	36.979	60.718	8.415	-0.409
4600	8.931	78.091	69.858	37.872	60.103	7.263	-0.345
4700	8.932	78.283	70.035	38.765	59.485	6.124	-0.285
4800	8.932	78.471	70.209	39.658	58.865	4.992	-0.227
4900	8.933	78.655	70.379	40.551	58.241	3.886	-0.173
4965	8.933	78.773	70.488	41.132	57.834	3.168	-0.139
4965	8.933	78.773	70.488	41.132	-83.463	3.168	-0.139
5000	8.933	78.836	70.547	41.445	-83.767	3.775	-0.165
5100	8.933	79.012	70.711	42.338	-84.663	5.534	-0.237
5200	8.934	79.186	70.872	43.231	-85.591	7.311	-0.307
5300	8.934	79.356	71.031	44.125	-86.549	9.111	-0.376
5400	8.934	79.523	71.186	45.018	-87.539	10.930	-0.442
5500	8.935	79.687	71.340	45.912	-88.557	12.760	-0.507
5600	8.935	79.848	71.490	46.805	-89.608	14.610	-0.570
5700	8.935	80.006	71.638	47.699	-90.688	16.484	-0.632
5800	8.935	80.162	71.784	48.592	-91.800	18.380	-0.693
5900	8.936	80.314	71.927	49.486	-92.943	20.278	-0.751
6000	8.936	80.465	72.068	50.379	-94.122	22.218	-0.809

Guggenheimer relation[411] and the estimated fundamental frequency of Swaminathan and Krishnamurty.[412] A value of 1.73 Å has also been estimated by Brewer and Chandrasekharaiah[413] who interpolated between values for the monoxides of transition metals. The 1.73 Å value was chosen for the present work.

2) Moment of inertia

The moment of inertia, I, was calculated from the above assumed value for the Mo–O bond distance by means of equation (188),

$$I = \mu r_o^2 = \left(\frac{M_{Mo}M_o}{M_{Mo} + M_o}\right) r_o^2 , \qquad (188)$$

wherein

μ = reduced mass

M_{Mo} = mass of molydbenum atom

M_o = mass of oxygen atom

and

r_o = Mo–O bond distance.

3) Fundamental frequency

The fundamental frequency, ω, of MoO had not been accurately determined. An approximate bond analysis by Swaminathan and Kristnamurty[412] yielded a value of 950 cm^{-1}. However, Brewer and Chandrasekharaiah[413] estimated this value to be 840 cm^{-1}. The value of 840 cm^{-1} was chosen for the present work as being more in accord with the postulate that the bonding in CrO is similar to that in MoO. Mass effects alone ($M_{Mo} > M_{Cr}$) would therefore indicate the choice of a lower fundamental frequency for MoO than for CrO. In view of the large uncertainty associated with the value of ω, no attempt was made to take into account anharmonicity effects and interaction terms. The thermodynamic functions given in Table LXII therefore apply to a rigid rotator-harmonic oscillator model.

411 Guggenheimer, K.M., Proc. Phys. Soc. (London) 58, 456 (1946).

412 Swaminathan, T.M. and S.G. Krishnamurty, Current Sci. 23, 258 (1954).

413 Brewer, L. and M.S. Chandrasekharaiah, U.S. AEC Rept. UCRL-8713 Rev. (June 1960).

4) Electronic states

The electronic states of MoO were unknown. The general practice, when no data are available, of considering only the ground state and assuming it to be a $^1\Sigma$ state was followed in this work. This procedure is simpler and is believed to be as correct as that used by other workers[410, 413] who have estimated electronic levels from a crude ionic central atom model.

The standard heat of formation of gaseous MoO at 298.15°K, $\Delta H^\circ_{f\,298}$, had not been directly determined. It was therefore determined by indirect methods. DeMaria and co-workers,[410] in a mass spectrographic study of Al_2O_3 using Mo crucibles, measured the partial pressures of MoO and monatomic oxygen in equilibrium with solid Mo at several temperatures in the range from 2200° to 2500°K. These measured pressures were used to obtain values for the equilibrium constant (K) of reaction (189).

$$Mo_{(s)} + O_{(g)} \rightarrow MoO_{(g)} \qquad (189)$$

$$K = \frac{P_{MoO_{(g)}}}{P_{O_{(g)}}} \; . \qquad (190)$$

The standard free-energy change, ΔF°, for this reaction at the several temperatures was evaluated by means of equation (191).

$$\Delta F^\circ = -RT \ln K_p \; . \qquad (191)$$

The value of ΔH°_{298} for reaction (189) was then obtained by means of equation (192).

$$\frac{\Delta H^\circ_{298}}{T} = \frac{\Delta F^\circ}{T} - \left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)_{MoO_{(g)}} + \left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)_{Mo_{(s)}} + \left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)_{O_{(g)}} \; . \qquad (192)$$

The values of the free-energy functions for $MoO_{(g)}$, $Mo_{(s)}$, and $O_{(g)}$ were taken from Tables LXII, XXVIII, and XXV of this report. A value for ΔH°_{298} was calculated at each temperature for which DeMaria and coworkers[410] reported measured pressures. The average of all the ΔH°_{298} values was combined with the ΔH°_{298} of dissociation of oxygen gas (O_2) to yield the heat of formation of gaseous MoO in accordance with the reaction scheme

$$Mo_{(s)} + O_{(g)} \rightarrow MoO_{(g)} \tag{193}$$

$$\tfrac{1}{2}O_{2(g)} \rightarrow O_{(g)} \tag{194}$$

$$Mo_{(s)} + \tfrac{1}{2}O_{2(g)} \rightarrow MoO_{(g)} \tag{195}$$

The value of the heat of formation so obtained was 87400 $\pm$ 5000 cal/gfw. The value of $H^\circ_{298} - H^\circ_0$ for MoO was found to be 2116 cal/gfw.

The values of ΔH°_f, ΔF°_f, and $\log_{10} K_p$ were than evaluated from the value of ΔH°_{f298} and equations (44), (196) and (197).

$$\Delta H^\circ_f = \Delta H^\circ_{f298} + (H^\circ_T - H^\circ_{298})_{MoO_{(g)}} - (H^\circ_T - H^\circ_{298})_{Mo_{(s)}} - \tfrac{1}{2}(H^\circ_T - H^\circ_{298})_{O_{2(g)}} \tag{196}$$

$$\Delta F^\circ_f = \Delta H^\circ_{f298} + (F^\circ_T - H^\circ_{298})_{MoO_{(g)}} - (F^\circ_T - H^\circ_{298})_{Mo_{(s)}} - \tfrac{1}{2}(F^\circ_T - H^\circ_{298})_{O_{2(g)}} . \tag{197}$$

The statement concerning the approximate nature of the functions for CrO_2 and CrO_3 in Tables LVIII and LIX also applies to those for MoO in Table LXII.

b. Molydbenum Dioxide (MoO_2)

1) Solid state

Thermodynamic properties of solid MoO_2, based on the low-temperature heat capacity measurements of King,[414] the high-temperature enthalpy data of King, Weller, and Christensen,[415] and the heat-of-formation data of Mah[416] have been reported.

[414] King, E.G., J. Am. Chem. Soc. 80, 1799 (1959).

[415] King, E.G., W.W. Weller, and A.V. Christensen, U.S. Bur. Mines Rept. Inv. 5664 (1960).

[416] Mah, A.D., J. Phys. Chem. 61, 1572 (1957).

The only experimental investigation of the low-temperature heat capacity of MoO_2 was that of King[414] which extended from 53° to 296°K. The value of $S^\circ_{298.15}$ obtained from these experimental data was 11.06 ± 0.05 e.u./gfw.

King, Weller, and Christensen[415] had reported the only experimental enthalpy values for MoO_2 at high temperatures (400° to 1800°K). The enthalpy functions for solid MoO_2 in Table LXIII are accordingly the smoothed values reported by King and coworkers[415] after extrapolation to 2000°K and to room temperature.

The tabular entropy values for solid MoO_2 were calculated from the enthalpy functions by the method of Kelley.[56]

Values for the free-energy function were calculated from equation (108). Tabular values of C°_p (in cal/°K gfw) were calculated from equation (198) due to King and co-workers.[415]

$$C^\circ_p = 14.11 + 5.82 \times 10^{-3}T - 2.18 \times 10^{+5}T^{-2} . \tag{198}$$

MoO_2 does not exhibit a true melting point since disproportionation occurs to yield solid Mo and MoO_3 vapor (including MoO_3 polymeric species) before melting occurs.[417,418]

The standard heat of formation, ΔH°_{f298} of solid MoO_2 was recently determined by Mah[416] from experimental measurements of the heat of combustion of $Mo_{(s)}$ to $MoO_{3(s)}$ and of $MoO_{2(s)}$ to $MoO_{3(s)}$. These measurements led directly to the heat of formation of $MoO_{2(s)}$. Mah obtained a value for ΔH°_{f298} of -140640 ± 130 cal/gfw, and after critical comparison of this value with earlier values,[419-423] recommended a value of -140800 ± 200 cal/gfw. This recommended value was accepted in the present compilation.

Values of ΔH°_f, ΔF°_f and $\log_{10} K_p$ were calculated from equations (44), (199), and (200).

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[417] Blackburn, P.E., M. Hoch, and H.L. Johnston, J. Phys. Chem. 62, 769 (1958).

[418] Burns, R.P., G. DeMaria, J. Drowart, and R.T. Grimley, J. Chem. Phys. 32, 1363 (1960).

[419] Staskiewicz, B.A., J.R. Tucker, and P.E. Snyder, J. Am. Chem. Soc. 77, 2987 (1955).

[420] Mixter, W.G., Am. J. Sci. 29, 488 (1910).

[421] Chaudron, G., Ann. Chim. 16, 221 (1921).

[422] Tonosaki, K., Bull. Inst. Phys. Chem. Research (Tokyo) 19, 126 (1940).

[423] Gokcen, N.A., J. Metals 5, 1019 (1953).

TABLE LXIII

MOLYBDENUM DIOXIDE CONDENSED PHASE MoO_2

Reference State for Calculating ΔH_f°, ΔF_f°, and Log K_p :
Solid Mo; Gaseous O_2; Solid MoO_2.

gfw = 127.95

T, °K	cal/°K gfw C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	Kcal/gfw $H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-1.995	-139.628	-139.628	Infinite
298.15	13.380	11.060	11.060	0.000	-140.800	-127.450	93.419
300	13.421	11.143	11.060	0.025	-140.799	-127.367	92.782
400	15.075	15.232	11.607	1.450	-140.668	-122.906	67.150
500	16.148	18.730	12.690	3.020	-140.437	-118.489	51.789
600	16.996	21.774	13.957	4.690	-140.145	-114.128	41.569
700	17.739	24.468	15.268	6.440	-139.807	-109.817	34.285
800	18.425	26.898	16.573	8.260	-139.425	-105.559	28.836
900	19.079	29.112	17.845	10.140	-139.009	-101.350	24.610
1000	19.712	31.145	19.075	12.070	-138.567	-97.189	21.240
1100	20.332	33.022	20.258	14.040	-138.116	-93.073	18.491
1200	20.943	34.781	21.398	16.060	-137.644	-89.000	16.208
1300	21.547	36.429	22.491	18.120	-137.161	-84.968	14.284
1400	22.147	37.992	23.542	20.230	-136.655	-80.972	12.640
1500	22.743	39.503	24.555	22.420	-136.085	-77.013	11.220
1600	22.337	41.007	25.538	24.750	-135.412	-73.096	9.984
1700	23.929	42.565	26.494	27.320	-134.532	-69.231	8.900
1800	24.519	44.256	27.434	30.280	-133.295	-65.425	7.943
1900	25.108	46.180	28.369	33.840	-131.493	-61.701	7.097
2000	25.695	48.457	29.317	38.280	-128.848	-58.094	6.348

$$\Delta F_f^\circ = \Delta H_{f298}^\circ + (F_T^\circ - H_{298}^\circ)_{MoO_{2(s)}} - (F_T^\circ - H_{298}^\circ)_{Mo_{(s)}} - (F_T^\circ - H_{298}^\circ)_{O_{2(g)}} \quad , \tag{199}$$

$$\Delta H_f^\circ = \Delta H_{f298}^\circ + (H_T^\circ - H_{298}^\circ)_{MoO_{2(s)}} - (H_T^\circ - H_{298}^\circ)_{Mo_{(s)}} - (H_T^\circ - H_{298}^\circ)_{O_{2(g)}} \quad . \tag{200}$$

2) Gaseous Phase

No experimental spectroscopic data had been reported for gaseous MoO_2 . All of the molecular constants required in the calculation of its thermodynamic functions were therefore estimated. The thermodynamic functions for gaseous MoO_2 given in Table LXIV were calculated by means of the machine program described in section III-F with the following molecular data:

Molecular configuration

Symmetric, nonlinear molecule with

$$\angle \text{O-Mo-O} = 107 \text{ deg}$$

$$r_o = 1.73 \text{ Å} \ .$$

Product of moments of inertia

$$I_A I_B I_C = 628260 \times 10^{-120} \text{ g}^3\text{cm}^6 \ .$$

Symmetry number

$$\theta = 2 \ .$$

Fundamental frequencies

$$\omega_1 = 824 \text{ cm}^{-1}$$

$$\omega_2 = 367 \text{ cm}^{-1}$$

$$\omega_3 = 857 \text{ cm}^{-1} \ .$$

Ground electronic state

$$^1\Sigma \ .$$

TABLE LXIV

MOLYBDENUM DIOXIDE — IDEAL MOLECULAR GAS — MoO_2

Reference State for Calculating ΔH_f°, ΔF_f°, and Log K_p : Solid Mo from 298.15° to 2890°K, Liquid Mo from 2890° to 4965°K, Gaseous Mo from 4965° to 6000°K; Gaseous O_2; Gaseous MoO_2

gfw = 127.95

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-2.670	0.297	0.297	Infinite
298.15	10.663	63.874	63.874	0.000	-0.200	-2.596	1.903
300	10.683	63.940	63.874	0.020	-0.204	-2.611	1.902
400	11.624	67.151	64.306	1.138	-0.380	-3.386	1.850
500	12.256	69.817	65.149	2.334	-0.523	-4.118	1.800
600	12.677	72.091	66.121	3.582	-0.653	-4.826	1.758
700	12.962	74.068	67.118	4.865	-0.782	-5.513	1.721
800	13.162	75.813	68.098	6.172	-0.913	-6.179	1.688
900	13.307	77.372	69.044	7.496	-1.053	-6.829	1.658
1000	13.414	78.780	69.948	8.832	-1.205	-7.462	1.631
1100	13.496	80.062	70.810	10.178	-1.378	-8.081	1.605
1200	13.559	81.240	71.631	11.531	-1.573	-8.681	1.581
1300	13.609	82.327	72.412	12.889	-1.792	-9.265	1.558
1400	13.649	83.337	73.157	14.252	-2.033	-9.832	1.535
1500	13.682	84.280	73.867	15.619	-2.286	-10.379	1.512
1600	13.709	85.164	74.546	16.988	-2.574	-10.909	1.490
1700	13.731	85.995	75.195	18.360	-2.892	-11.422	1.468
1800	13.750	86.781	75.817	19.734	-3.241	-11.912	1.446
1900	13.767	87.525	76.414	21.110	-3.623	-12.384	1.424
2000	13.780	88.231	76.987	22.488	-4.040	-12.834	1.402
2100	13.792	88.904	77.539	23.866	-4.496	-13.264	1.380
2200	13.803	89.546	78.070	25.246	-4.990	-13.669	1.358
2300	13.812	90.160	78.583	26.627	-5.524	-14.053	1.335
2400	13.820	90.748	79.077	28.008	-6.102	-14.410	1.312
2500	13.827	91.312	79.556	29.391	-6.725	-14.745	1.289
2600	13.833	91.854	80.018	30.774	-7.394	-15.051	1.265
2700	13.839	92.376	80.466	32.157	-8.112	-15.333	1.241
2800	13.844	92.880	80.901	33.541	-8.878	-15.585	1.216
2890	13.848	93.317	81.271	34.788	-9.612	-15.762	1.192
2890	13.848	93.317	81.271	34.788	-16.262	-15.762	1.192
2900	13.848	93.366	81.322	34.926	-16.319	-15.785	1.190
3000	13.852	93.835	81.732	36.311	-16.886	-15.759	1.148
3100	13.856	94.290	82.129	37.696	-17.458	-15.708	1.107
3200	13.859	94.729	82.516	39.082	-18.034	-15.648	1.069
3300	13.862	95.156	82.893	40.468	-18.613	-15.563	1.031
3400	13.865	95.570	83.260	41.855	-19.196	-15.463	0.994
3500	13.868	95.972	83.617	43.241	-19.784	-15.341	0.958
3600	13.870	96.363	83.966	44.628	-20.375	-15.206	0.923
3700	13.872	96.743	84.306	46.015	-20.969	-15.052	0.889
3800	13.874	97.113	84.638	47.403	-21.566	-14.885	0.856
3900	13.876	97.473	84.963	48.790	-22.168	-14.703	0.824
4000	13.878	97.824	85.280	50.178	-22.722	-14.500	0.792
4100	13.879	98.167	85.590	51.566	-23.380	-14.289	0.762
4200	13.881	98.501	85.893	52.954	-23.992	-14.057	0.731
4300	13.882	98.828	86.190	54.342	-24.607	-13.807	0.702
4400	13.884	99.147	86.481	55.730	-25.227	-13.548	0.673
4500	13.885	99.459	86.766	57.119	-25.849	-13.280	0.645
4600	13.886	99.764	87.046	58.507	-26.477	-12.990	0.617
4700	13.887	100.063	87.319	59.896	-27.109	-12.690	0.590
4800	13.888	100.355	87.588	61.284	-27.748	-12.374	0.563
4900	13.889	100.642	87.851	62.673	-28.392	-12.044	0.537
4965	13.890	100.824	88.019	63.576	-28.816	-11.817	0.520
4965	13.890	100.824	88.019	63.576	-170.113	-11.817	0.520
5000	13.890	100.922	88.110	64.062	-170.426	-10.705	0.468
5100	13.890	101.198	88.364	65.451	-171.351	-7.502	0.321
5200	13.891	101.467	88.613	66.840	-172.313	-4.280	0.180
5300	13.892	101.732	88.858	68.229	-173.312	-1.039	0.043
5400	13.893	101.992	89.099	69.619	-174.349	2.225	-0.090
5500	13.893	102.246	89.336	71.008	-175.425	5.511	-0.219
5600	13.894	102.497	89.569	72.397	-176.543	8.803	-0.344
5700	13.895	102.743	89.798	73.787	-177.703	12.135	-0.465
5800	13.895	102.984	90.023	75.176	-178.911	15.480	-0.496
5900	13.896	103.222	90.245	76.566	-180.169	18.839	-0.698
6000	13.896	103.455	90.463	77.955	-181.484	22.236	-0.810

a) Molecular configuration

The molecular configuration of MoO_2 was unknown. Consideration of the periodic group to which molybdenum belongs and the work of Walsh[395] on bonding and structural relations led to the conclusion that MoO_2 is a symmetric, nonlinear molecule. It therefore was so considered in the present work. DeMaria and co-workers[410] also assumed it to have a nonlinear structure, whereas Chandrasekharaiah and Brewer[397] assumed it to have the linear structure of all of the Group IV, V, and VI transition metal dioxides.

An O–Mo–O angle of 107 degrees was chosen in the present work as representing a reasonable value in comparison with known compounds of similar bonding.

The Mo–O bond distance was assumed to be identical to the estimated corresponding distance for the molybdenum monoxide (MoO) molecule; i. e., 1.73Å.

b) Moments of inertia

The moments of inertia of MoO_2 were calculated in a manner analogous to that used for the corresponding CrO_2 molecule.

c) Fundamental frequencies

The fundamental frequencies of MoO_2 were estimated by the same method used for the corresponding CrO_2 molecule (see section IV-B3a above), except that the stretching force constant for MoO was calculated from estimated spectroscopic data.[413] The frequencies so obtained are somewhat lower than those estimated by DeMaria and co-workers.[410]

d) Electronic states

The electronic states for MoO_2 were treated in the same manner as those of the CrO_2 molecule.

The standard enthalpy of formation, ΔH°_{f298}, of gaseous MoO_2 had not been directly determined but could be indirectly evaluated by two different calculations. The first calculation was based on results of the mass spectrographic study of Al_2O_3 reported by DeMaria and co-workers[410] using molybdenum crucibles. These workers measured the partial pressures of MoO_2 and monatomic oxygen in equilibrium with solid molybdenum at several temperatures in the range from 2200° to 2500°K. From these pressures, the equilibrium constant, K, in equation (202) and the standard free energy change, $\Delta F°$, for reaction (201) could be calculated

$$Mo_{(s)} + 2O_{(g)} \longrightarrow MoO_{2(g)} \tag{201}$$

$$K = \frac{P_{MoO_{2(g)}}}{P^2_{O_{(g)}}} , \tag{202}$$

as explained in the preceding section of the report concerning MoO.

A value of ΔH°_{298} for the above reaction at each temperature for which measured pressures were reported was then calculated by the Third Law Method, which assumes the form of equation (203).

$$\frac{\Delta H^\circ_{298}}{T} = \frac{\Delta F^\circ}{T} - \left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)_{MoO_{2(g)}} + \left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)_{Mo_{(s)}} + 2\left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)_{O_{(g)}} . \tag{203}$$

The values of the free-energy functions for $MoO_{2(g)}$, $Mo_{(s)}$, and $O_{(g)}$ were taken from Tables LXIV, XXVIII, and XXV of this report. The average of all the ΔH°_{298} values for reaction (201) was then combined with the ΔH°_{298} of dissociation of oxygen gas (O_2) to yield the heat of formation of gaseous MoO_2 in accordance with the reaction scheme

$$Mo_{(s)} + 2O_{(g)} \longrightarrow MoO_{2(g)} \tag{204}$$

$$O_{2(g)} \longrightarrow 2O_{(g)} \tag{205}$$

$$Mo_{(s)} + O_{2(g)} \longrightarrow MoO_{2(g)} . \tag{206}$$

The first value of the heat of formation of MoO_2 gas so obtained was 5380 ± 4500 cal/gfw at 298.15°K.

The second calculation was based on results of the mass spectrographic study of the gaseous species in equilibrium with solid MoO_2 reported by Burns and co-workers.[418] Partial pressures of $MoO_{2(g)}$ in equilibrium with $MoO_{2(s)}$ were reported at several temperatures in the range from 1560° to $1780^{\circ}K$. From these measured pressures, the standard free-energy change, ΔF°, for the sublimation of MoO_2 as in reaction (207) could be calculated at each temperature.

$$MoO_{2(s)} \longrightarrow MoO_{2(g)} , \qquad (207)$$

by means of equation (208),

$$\Delta F^{\circ} = - RT \ln P_{MoO_{2(g)}} \qquad (208)$$

values of ΔH°_{298} corresponding to each calculated ΔF° value were then calculated from equation (129).

The values of the free-energy function used for $MoO_{2(s)}$ and $MoO_{2(g)}$ were taken from Tables LXIII and LXIV of this report. The average of all values of ΔH°_{298} for reaction (207) was combined with the heat of formation of solid MoO_2 to yield the heat of formation of gaseous MoO_2 in accordance with the reaction scheme at $298.15^{\circ}K$.

$$MoO_{2(s)} \longrightarrow MoO_{2(g)} \qquad (209)$$

$$Mo_{(s)} + O_{2(g)} \longrightarrow MoO_{2(s)} \qquad (210)$$

$$Mo_{(s)} + O_{2(g)} \longrightarrow MoO_{2(g)} \qquad (211)$$

The second value of the heat of formation of MoO_2 gas so obtained was -5700 ± 2000 cal/gfw. The average of the two values, after rounding off to the nearest hundred calories, was -200 ± 6000 cal/gfw. The value of $H^{\circ}_{298} - H^{\circ}_{0}$ for $MoO_{2(g)}$ was found to be 2670 cal/gfw.

Values of ΔH°_{f}, ΔF°_{f}, and $\log_{10} K_p$ were calculated by methods already described.

c. Molybdenum Trioxide (MoO_3)

1) Condensed phase

a) Melting point and heat of fusion

The melting point of MoO_3 had been determined by Hoermann[424] (1068°K), Cosgrove and Snyder[425] (1068°K), Babadzhan[426] (1070°K), and King, Weller, and Christensen[415] (1074°K). The average value of 1070° ± 5°K was adopted for the present compilation.

The heat of fusion, as determined from enthalpy values of the solid and liquid at the melting point, was 11,683 cal/gfw. An uncertainty of 500 cal/gfw was arbitrarily assigned to this heat of fusion. The ΔH value is almost identical to that reported by King, Weller, and Christensen[415] (11,690 cal/gfw), but appreciably lower than the value reported by Cosgrove and Snyder[425] (12,540 cal/gfw).

b) Boiling point

The equilibrium vapor above MoO_3 consists primarily of $(MoO_3)_3$, $(MoO_3)_4$, and $(MoO_3)_5$ according to Berkowitz, Inghram, and Chupka.[427] Evidence for the existence of polymeric MoO_3 vapor species is also furnished by the work of Blackburn, Hoch, and Johnston,[417] Babadzhan,[426] and of Zelikman, Gorovits, and Prosenkova.[428] No attempt has been made in the present work to define a boiling point for MoO_3. A temperature of about 1450°K had been quoted[264] as the temperature at which the total pressure above MoO_3 becomes one atmosphere. No attempt was made to estimate thermodynamic functions for these polymeric vapor species because of the lack of basic data.

[424] Hoermann, F., Z. anorg. u. allgem. Chem. 177, 145 (1928).

[425] Cosgrove, L. A. and P. E. Snyder, J. Am. Chem. Soc. 75, 1227 (1953).

[426] Babadzhan, A. A., Trudy Inst. Met., Akad. Nauk SSSR Ural. Filial, Sbornik Rabot 1, 74 (1957).

[427] Berkowitz, J., M. G. Inghram, and W. A. Chupka, J. Chem. Phys. 26, 842 (1957).

[428] Zelikman, A. N., N. N. Gorovits, and T. E. Prosenkova, Zhur. Neorg. Khim. 1, 632 (1956).

c) Entropy at 298.15° K (S^o_{298})

Kelley and King[318] recommended 18.58 $\pm$ 0.10 e.u./gfw as the value of S^o_{298} for MoO_3. This value was based on the low-temperature heat capacity measurements of Seltz, Dunkerley, and DeWitt,[429] and of Smith, Brown, Dworkin, Sasmor, and Van Artsdalen.[430]

d) Thermodynamic functions for the condensed state

Enthalpy measurements by dropping methods have been reported by Cosgrove and Snyder[425] (300° to 1300°K) and by King, Weller, and Christensen[415] (400° to 1400°K). The results of the latter workers were arbitrarily chosen for this compilation. The results reported by Cosgrove and Snyder[425] were about 2 percent higher than the former results.

The C^o_p values (in cal/°K gfw) for solid MoO_3 from 298.15°K to the melting point (1070°K) given in Table LXV were calculated by means of equation (212) given by King, Weller and Christensen.[415]

$$C^o_p = 17.97 + 7.80 \times 10^{-3}T - 2.10 \times 10^5 T^{-2}. \qquad (212)$$

The derived equations used to calculate the enthalpy and entropy functions for solid MoO_3 were

$$H^o_T - H^o_{298} = 17.97T + 390.0 \times 10^{-5}T^2 + 2.10 \times 10^5 T^{-1} - 6409 \qquad (213)$$

$$S^o_T = 17.97 \ln T + 7.80 \times 10^{-3}T + 1.05 \times 10^5 T^{-2} - 87.313. \qquad (214)$$

Values for the free-energy function were calculated by means of equation (108).

The heat capacity of liquid MoO_3 was reported to be constant at 30.20 cal/°K gfw by King and co-workers.[415] This value was chosen in the present work in preference to the rather

[429] Seltz, H., F. J. Dunkerley, and B. J. DeWitt, J. Am. Chem. Soc. 65, 600 (1943).

[430] Smith, D. F., D. Brown, A. S. Dworkin, D. J. Sasmor, and E. R. Van Artsdalen, J. Am. Chem. Soc. 78, 1533 (1956).

TABLE LXV

MOLYBDENUM TRIOXIDE — CONDENSED PHASES — MoO_3

Reference State for Calculating ΔH_f°, ΔF_f°, and $\mathrm{Log}\ K_p$: Solid Mo; Gaseous O_2; Solid MoO_3 from 298.15° to 1070° K, Liquid MoO_3 from 1070° to 1500° K.

gfw = 143.95 — m.p. = 1070° ± 5° K

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	$\mathrm{Log}\ K_p$
0	0.000	0.000	Infinite	-3.009	-176.905	-176.905	Infinite
298.15	17.934	18.580	18.580	0.000	-178.100	-159.686	117.048
300	17.977	18.691	18.581	0.033	-178.098	-159.572	116.243
400	19.777	24.130	19.310	1.928	-177.851	-153.431	83.827
500	21.030	28.684	20.742	3.971	-177.513	-147.361	64.408
600	22.067	32.612	22.400	6.127	-177.113	-141.369	51.491
700	23.001	36.084	24.111	6.381	-176.659	-135.447	42.286
800	23.882	39.213	25.805	10.726	-176.152	-129.593	35.401
900	24.731	42.076	27.457	13.157	-175.591	-123.807	30.063
1000	25.560	44.724	29.053	15.671	-174.979	-118.084	25.806
1070	26.133	46.473	30.136	17.481	-174.526	-114.123	23.309
1070	30.200	57.392	30.136	29.164	-162.843	-114.123	23.309
1100	30.200	58.227	30.891	30.070	-162.519	-112.756	22.401
1200	30.200	60.855	33.280	33.090	-161.471	-108.277	19.719
1300	30.200	63.272	35.495	36.110	-160.456	-103.887	17.464
1400	30.200	65.511	37.561	39.130	-159.472	-99.576	15.544
1500	30.200	67.594	39.494	42.150	-158.508	-95.331	13.889

unexpected values reported by Cosgrove and Snyder.[425]

$H^\circ_T - H^\circ_{298}$, S°_T , and $-\left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)$ for liquid MoO_3 were then calculated by means of equations (215), (216), and (108).

$$H^\circ_T - H^\circ_{298} = 30.20T - 3150 \tag{215}$$

$$S^\circ_T = 30.20 \ln T - 153.265 . \tag{216}$$

e) Standard heat of formation at 298.15°K (ΔH°_{f298})

The standard heat of formation, ΔH°_{f298} , of solid MoO_3 was recently determined by Mah,[416] from experimental measurements of the heat of combustion of $Mo_{(s)}$ to $MoO_{3(s)}$, to be -178,160 ± 110 cal/gfw. From a comparison of this value with that of earlier workers,[419, 420, 431-433] Mah[416] chose a "recommended" value of -178,100 ± 100 cal/gfw. This "recommended" value was adopted in the present compilation.

The values of ΔH°_f , ΔF°_f , and $\log_{10}K_p$ were than calculated according to equations (217), (218), and (44).

$$\Delta F^\circ_f = \Delta H^\circ_{f298} + (F^\circ_T - H^\circ_{298})_{MoO_{3(c)}} - (F^\circ_T - H^\circ_{298})_{Mo_{(s)}}$$
$$- 3/2 (F^\circ_T - H^\circ_{298})_{O_{2(g)}} \tag{217}$$

$$\Delta H^\circ_f = \Delta H^\circ_{f298} + (H^\circ_T - H^\circ_{298})_{MoO_{3(c)}} - (H^\circ_T - H^\circ_{298})_{Mo_{(s)}}$$
$$- 3/2 (H^\circ_T - H^\circ_{298})_{O_{2(g)}} . \tag{218}$$

2) Gaseous phase

No experimental spectroscopic data had been reported for gaseous MoO_3 . All of the molecular constants required in the calculation of the thermodynamic functions were therefore estimated. The thermodynamic functions for gaseous MoO_3 given in Table LXVI were calculated by means of the machine program described in section III-F with the following molecular data:

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[431]Delepine, M., Bull. Soc. Chim. 29, 1166 (1903).

[432]Moose, J. E. and S. W. Parr, J. Am. Chem. Soc. 46, 2656 (1924).

[433]Newmann, B., C. Kroger, and H. Kunz, A. anorg. u. allgem. Chem. 218, 379 (1934).

TABLE LXVI

MOLYBDENUM TRIOXIDE — IDEAL MOLECULAR GAS — MoO_3

Reference State for Calculating ΔH_f°, ΔF_f°, and Log K_p : Solid Mo from 298.15° to 2890°K, Liquid Mo from 2890° to 4965°K, Gaseous Mo from 4965° to 6000°K; Gaseous O_2; Gaseous MoO_3.

gfw = 143.95 m.p. = 1070° ± 5°K

T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
	cal/°K gfw			Kcal/gfw			
0	0.000	0.000	Infinite	-3.227	-80.023	-80.023	Infinite
298.15	14.498	66.653	66.653	0.000	-81.000	-76.919	56.381
300	14.533	66.742	66.653	0.027	-81.004	-76.894	56.014
400	16.105	71.153	67.244	1.564	-81.115	-75.504	41.252
500	17.147	74.867	68.407	3.230	-81.154	-74.094	32.385
600	17.838	78.059	69.756	4.982	-81.158	-72.682	26.473
700	18.308	80.846	71.145	6.790	-81.150	-71.271	22.251
800	18.637	83.313	72.515	8.639	-81.139	-69.861	19.084
900	18.876	85.523	73.840	10.515	-81.133	-68.451	16.621
1000	19.052	87.521	75.110	12.412	-81.138	-67.041	14.651
1100	19.186	89.344	76.322	14.324	-81.165	-65.629	13.039
1200	19.291	91.018	77.478	16.248	-81.213	-64.216	11.695
1300	19.374	92.565	78.580	18.18	-81.285	-62.798	10.557
1400	19.440	94.004	79.631	20.122	-81.380	-61.373	9.580
1500	19.494	95.347	80.634	22.069	-81.489	-59.940	8.733
1600	19.539	96.606	81.593	24.021	-81.632	-58.496	7.990
1700	19.576	97.792	82.512	25.977	-81.808	-57.049	7.334
1800	19.607	98.912	83.392	27.936	-82.016	-55.586	6.749
1900	19.634	99.973	84.237	29.898	-82.259	-54.110	6.224
2000	19.657	100.981	85.049	31.862	-82.540	-52.620	5.750
2100	19.677	101.940	85.831	33.829	-82.860	-51.116	5.319
2200	19.694	102.856	86.584	35.798	-83.221	-49.597	4.927
2300	19.709	103.732	87.311	37.768	-83.624	-48.059	4.566
2400	19.722	104.571	88.013	39.739	-84.072	-46.507	4.235
2500	19.734	105.376	88.691	41.712	-84.569	-44.930	3.928
2600	19.744	106.150	89.348	43.686	-85.113	-43.334	3.642
2700	19.753	106.896	89.984	45.661	-85.709	-41.715	3.376
2800	19.762	107.614	90.601	47.637	-86.353	-40.071	3.128
2890	19.768	108.239	91.140	49.415	-86.983	-38.576	2.917
2890	19.768	108.239	91.140	49.415	-93.633	-38.576	2.917
2900	19.769	108.308	91.200	49.613	-93.577	-38.384	2.893
3000	19.776	108.978	91.781	51.590	-94.128	-36.468	2.657
3100	19.782	109.626	92.346	53.568	-94.586	-34.531	2.434
3200	19.787	110.255	92.896	55.547	-95.050	-32.598	2.226
3300	19.792	110.864	93.432	57.526	-95.518	-30.634	2.029
3400	19.797	111.455	93.953	59.505	-95.995	-28.665	1.843
3500	19.801	112.028	94.461	61.485	-96.475	-26.670	1.665
3600	19.805	112.586	94.957	63.466	-96.962	-24.667	1.497
3700	19.809	113.129	95.441	65.446	-97.453	-22.655	1.338
3800	19.812	113.657	95.913	67.427	-97.949	-20.626	1.186
3900	19.815	114.172	96.375	69.409	-98.451	-18.584	1.041
4000	19.818	114.674	96.826	71.390	-98.958	-16.528	0.903
4100	19.821	115.163	97.267	73.372	-99.470	-14.461	0.771
4200	19.823	115.641	97.699	75.354	-99.988	-12.382	0.644
4300	19.825	116.107	98.122	77.337	-100.509	-10.281	0.523
4400	19.827	116.563	98.536	79.319	-101.040	-8.180	0.406
4500	19.829	117.009	98.941	81.302	-101.573	-6.066	0.295
4600	19.831	117.444	99.339	83.285	-102.114	-3.933	0.187
4700	19.833	117.871	99.729	85.269	-102.662	-1.791	0.083
4800	19.835	118.289	100.111	87.252	-103.219	0.370	-0.017
4900	19.836	118.698	100.486	89.235	-103.786	2.533	-0.113
4965	19.837	118.958	100.725	90.525	-104.161	3.957	-0.174
4965	19.837	118.958	100.725	90.525	-245.458	3.957	-0.174
5000	19.838	119.098	100.854	91.219	-245.745	5.710	-0.250
5100	19.839	119.491	101.216	93.203	-246.600	10.746	-0.460
5200	19.840	119.876	101.571	95.187	-247.497	15.798	-0.664
5300	19.841	120.254	101.920	97.171	-248.438	20.871	-0.861
5400	19.843	120.625	102.263	99.155	-249.245	25.969	-1.051
5500	19.844	120.989	102.600	101.139	-250.458	31.086	-1.235
5600	19.845	121.347	102.932	103.124	-251.544	36.210	-1.413
5700	19.846	121.698	103.256	105.108	-252.686	41.371	-1.586
5800	19.847	122.043	103.579	107.093	-253.890	46.551	-1.754
5900	19.847	122.383	103.895	109.078	-255.163	51.737	-1.916
6000	19.848	122.716	104.206	111.063	-256.515	56.964	-2.075

Molecular configuration

Planar, symmetrical, cart-wheel molecule with

$\angle O - Mo - O = 120$ deg.

$r_o = 1.73\text{Å}$.

Product of moments of inertia

$I_A I_B I_C = 3392032 \times 10^{-120} g^3 cm^6$.

Symmetry number

$\sigma = 6$.

Fundamental frequencies

$\omega_1 = 800\ cm^{-1}$

$\omega_2 = 344\ cm^{-1}$

$\omega_3 = 897\ cm^{-1}$ (2)

$\omega_4 = 317\ cm^{-1}$ (2).

Ground electronic state

$^1\Sigma$

These molecular constants were estimated by the procedures employed in the case of the corresponding CrO_3 molecule (see section IV-B3b). The Mo - O bond distance was assumed to be the same as the estimated distance for the corresponding bond in MoO[413]; i.e., 1.73Å.

The standard enthalpy of formation, ΔH^o_{f298}, of gaseous MoO_3 had not been directly determined but could be indirectly evaluated by two calculations similar to those described in connection with MoO_2; see section IV-B5c(2).

The first calculation was based on the mass spectrographic study of Al_2O_3 reported by DeMaria and co-workers[410] using molybdenum crucibles. These workers measured the partial pressures of MoO_3 and monatomic oxygen in equilibrium with solid molybdenum at several temperatures in the range from 2200° to 2500°K. From the partial pressures of these workers, the equilibrium constant, K , and the standard free-energy change, ΔF° , for reaction (219) could be evaluated

$$Mo_{(s)} + 3O_{(g)} \longrightarrow MoO_{3(g)} \tag{219}$$

$$K = \frac{P_{MoO_{3(g)}}}{P^3_{O_{(g)}}} \tag{220}$$

as explained in section IV-B5a for the case of MoO .

A value of ΔH°_{298} for the above reaction was calculated at each temperature for which a measured pressure was reported by the Third Law Method as explained in section IV-B5a which takes the form of equation (221).

$$\frac{\Delta H^\circ_{298}}{T} = \frac{\Delta F^\circ}{T} - \left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)_{MoO_{3(g)}} + \left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)_{Mo_{(s)}} + 3\left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)_{O_{(g)}} . \tag{221}$$

The values of the free-energy functions for $MoO_{3(g)}$, $Mo_{(s)}$ and $O_{(g)}$ were taken from Tables LXVI, XXVIII, and XXV of this report. The average value of ΔH°_{298} was then combined with the heat of dissociation of oxygen gas (O_2) to yield the heat of formation of gaseous MoO_3 , in accordance with the reaction scheme at 298.15°K

$$Mo_{(s)} + 3O_{(g)} \longrightarrow MoO_{3(g)} \tag{222}$$

$$(3/2)\,O_{2(g)} \longrightarrow 3O_{(g)} \tag{223}$$

$$Mo_{(s)} + (3/2)\,O_{2(g)} \longrightarrow MoO_{3(g)} \; . \tag{224}$$

The first value of the heat of formation so obtained was -77, 100 ± 3000 cal/gfw at 298.15°K.

Likewise the second calculation was based on the mass spectrographic study of the gaseous species above solid MoO_2 reported by

Burns and co-workers.[418] Partial pressures of $MoO_{3(g)}$ in equilibrium with $MoO_{2(s)}$ and $Mo_{(s)}$ were reported at several temperatures in the range from 1560° to 1780°K. From these measured pressures, the standard free-energy change, ΔF°, at each temperature was calculated for reaction (225)

$$(3/2)\,MoO_{2(s)} \longrightarrow MoO_{3(g)} + (1/2)\,Mo_{(s)} \qquad (225)$$

by methods already described in connection with MoO and MoO_2. Values of ΔH°_{298} corresponding to each calculated ΔF° value calculated by means of equation (226).

$$\frac{\Delta H^\circ_{298}}{T} = \frac{\Delta F^\circ}{T} - \left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)_{MoO_{3(g)}} - (1/2)\left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)_{Mo_{(s)}}$$

$$+ (3/2)\left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)_{MoO_{2(s)}} \qquad (226)$$

The values of the free-energy functions used for $MoO_{3(g)}$, $Mo_{(s)}$ and $MoO_{2(s)}$ are given in Tables LXVI, XXVII, and LXIII of this report. The average of all the values of ΔH°_{298} for equation (225) was then combined with the heat of formation of solid MoO_2 to yield the heat of formation of gaseous MoO_3, in accordance with the reaction scheme at 298.15°K,

$$(3/2)\,MoO_{2(s)} \longrightarrow MoO_{3(g)} + (1/2)\,Mo_{(s)} \qquad (227)$$

$$(3/2)\,Mo_{(s)} + (3/2)\,O_{2(g)} \longrightarrow (3/2)\,MoO_{2(g)} \qquad (228)$$

$$Mo_{(s)} + (3/2)\,O_{2(g)} \longrightarrow MoO_{3(g)}\,. \qquad (229)$$

The second value of the heat of formation so obtained was -84,900 ± 1000 cal/gfw.

The average of the values obtained by two different methods for the heat of formation of gaseous MoO_3 was -81,000 ± 6000 cal/gfw. The value of $H^\circ_{298} - H^\circ_0$ for $MoO_{3(g)}$ was found to be 3227 cal/gfw.

Values of ΔH°_f, ΔF°_f, and $\log_{10} K_p$ were calculated by methods previously described.

6. Strontium Oxide (SrO)

a. Crystal Structure and Melting Point

Strontium oxide has a face-centered cubic ($NaCl$ type) structure[57] at room temperature which was assumed to persist to the melting point. The thermal expansion was measured by Beals and Cook[384] up to 1500°K. The melting point of SrO was taken as 2690° ± 50°K from the results of Schumacher[385] (corrected to the International Temperature Scale of 1948).

b. Thermodynamic Properties of the Condensed Phases

1) Heat of fusion

The heat of fusion of SrO was assumed to be 16.1 ± 1.4 Kcal/gfw from an estimated entropy of fusion of 5.985 ± 0.5 Kcal/°K gfw. Kubaschewski and Evans[182] estimated the entropy of fusion to be 6.1 Kcal/°K gfw.

2) Entropy and heat content at 298.15°K

The low-temperature heat capacity of SrO was measured by Anderson.[434] From these data, S^o_{298} was calculated to be 13.060 ± 0.200 cal/°K gfw. $H^o_{298}-H^o$ was found to be 2037.7 cal/gfw.

3) High-temperature heat content

The high-temperature heat content of SrO was measured by Lander[388] (298° to 1266°K). Kelley[56] fitted Lander's data in cal/gfw to equation (230).

$$H^o_T - H^o_{298} = 12.13T + 0.63 \times 10^{-3}T^2 + 1.55 \times 10^5/T - 4192 \quad (230)$$

Equation (230) was adopted here and extrapolated to the melting point. An uncertainty of ± 3 percent was assigned to the enthalpy.

The heat capacity of liquid SrO was estimated to be 17.0 cal/°K gfw.

Thermodynamic functions of the condensed phases of SrO are given in Table LXVII. Analyses of the heat-of-formation data had not been completed at the time of report writing. Uncertainty estimates are summarized on the back of the table.

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434 Anderson, C. T., J. Am. Chem. Soc. 57, 429 (1935).

c. Thermodynamic Properties of the Ideal Molecular Gas

The thermodynamic functions of SrO gas were calculated with the computer program based on the treatment of the diatomic molecule outlined in section III-E of this report. The spectroscopic constants used for the electronic states (in units of cm^{-1}) were:

Constant	$X'^1\Sigma$	$A'^1\Sigma$	$B'^1\Pi$	$C'^1\Sigma$
E	0	10885.0	24004.0	28546.4
ω_e	653.47	619.6	520.0	480.2
$\omega_e x_e$	3.95	0.9	3.5	2.6
$\omega_e y_e$	---	---	---	---
B_e	0.3379	0.3047	0.2936	0.2742
α_e	0.0021	0.0011	0.0020	0.0021
γ_e	---	---	---	---
$D_e(\times 10^6)$	0.42	3.2	0.37	0.35
g	1	1	2	1

The above spectroscopic constants were not corrected to those appropriate for a naturally occurring isotopic mixture. Constants for the assumed ground state were from Kovacs and Budo,[435] and were practically identical to those given by Lagerqvist and Selin.[436] Constants for the A' state were from Almkvist and Lagerqvist.[437] The data of Mahanti[438] and Lagerqvist[390] were used for the B'state, and those of Lagerqvist and Almkvist[439] were used for the C'state. The results of the computation are given in Table LXVIII. $H^\circ_{298}-H^\circ_0$ was calculated to be 2160.9 cal/gfw. Veits and Gurvich[394] tabulated thermodynamic functions of $SrO_{(g)}$ up to 3500°K using the first two electronic states

[435] Kovacs, I. and A. Budo, Ann. Physik 12, 17 (1953).

[436] Lagerqvist, A. and L.E. Selin, Ark. Fys. 11, 323 (1956).

[437] Almkvist, G. and A. Lagerqvist, Ark. Fys. 1, 477 (1949).

[438] Mahanti, P.C., Phys. Rev. 42, 609 (1932).

[439] Lagerqvist, A. and G. Almkvist, Ark. Fys. 8, 481 (1954).

TABLE LXVII

STRONTIUM OXIDE — CONDENSED PHASES — OSr

gfw = 103.63 — m.p. = 2690° ± 50°K

T, °K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal/gfw)	ΔH_f° (Kcal/gfw)	ΔF_f° (Kcal/gfw)	Log K_p
0	0.000	0.000	Infinite	-2.038			Infinite
298.15	10.760	13.060	13.060	0.000			
300	10.784	13.126	13.060	0.020			
400	11.663	16.365	13.495	1.148			
500	12.138	19.024	14.344	2.340			
600	12.453	21.267	15.316	3.571			
700	12.694	23.205	16.307	4.829			
800	12.894	24.914	17.278	6.108			
862	13.006	25.881	17.863	6.912			
862	13.006	25.881	17.863	6.912			
900	13.071	26.443	18.213	7.407			
1000	13.233	27.829	19.107	8.723			
1045	13.303	28.413	19.495	9.320			
1045	13.303	28.413	19.495	9.320			
1100	13.386	29.098	19.958	10.054			
1200	13.532	30.269	20.769	11.400			
1300	13.674	31.358	21.542	12.760			
1400	13.813	32.376	22.280	14.135			
1500	13.949	33.334	22.985	15.523			
1600	14.083	34.239	23.661	16.925			
1641	14.138	34.596	23.929	17.504			
1641	14.138	34.596	23.929	17.504			
1700	14.216	35.097	24.309	18.340			
1800	14.348	35.913	24.930	19.769			
1900	14.479	36.693	25.530	21.210			
2000	14.609	37.439	26.107	22.665			
2100	14.739	38.155	26.663	24.133			
2200	14.868	38.844	27.202	25.613			
2300	14.997	39.507	27.721	27.107			
2400	15.125	40.148	28.226	28.613			
2500	15.253	40.769	28.716	30.132			
2600	15.381	41.369	29.191	31.664			
2690	15.496	41.895	29.607	33.054			
2690	17.000	47.880	29.607	49.154			
2700	17.000	47.943	29.675	49.324			
2800	17.000	48.561	30.338	51.024			
2900	17.000	49.158	30.977	52.724			
3000	17.000	49.734	31.593	54.424			
3100	17.000	50.292	32.187	56.124			
3200	17.000	50.832	32.762	57.824			
3300	17.000	51.354	33.316	59.524			
3400	17.000	51.862	33.855	61.224			
3500	17.000	52.355	34.377	62.924			
3600	17.000	52.834	34.883	64.624			
3700	17.000	53.299	35.374	66.324			
3800	17.000	53.753	35.852	68.024			
3900	17.000	54.194	36.316	69.724			
4000	17.000	54.625	36.769	71.424			

STRONTIUM OXIDE CONDENSED PHASES

SUMMARY OF UNCERTAINTY ESTIMATES

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
298.15	± .200	± .200	± .200	± .000			
1000	± .940	± .650	± .390	± .260			
2000	±1.780	± .940	± .600	± .680			
2690	±2.680	±1.070	± .700	± .990			
2690	±1.000	±1.590	± .700	±2.390			
4000	±2.000	±2.190	±1.100	±4.350			

only. As in the case of the other alkaline earth oxides discussed in this report, the true ground state of SrO is in question. Further analysis of the effect of this uncertainty on the thermodynamic functions is required.

The review of the heat-of-formation data in the literature was not completed at the time of report writing.

TABLE LXVIII

STRONTIUM OXIDE — IDEAL MONATOMIC GAS — OSr

gfw = 103.63 m.p. = 2690° ± 50°K

T, °K	cal/°K gfw			Kcal/gfw			
	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-2.161			Infinite
298.15	7.910	54.961	54.961	0.000			
300	7.919	55.010	54.962	0.015			
400	8.309	57.342	55.277	0.826			
500	8.501	59.215	55.883	1.666			
600	8.644	60.778	56.572	2.523			
700	8.742	62.118	57.271	3.393			
800	8.813	63.291	57.952	4.271			
862	8.846	63.946	58.356	4.819			
862	8.846	63.946	58.356	4.819			
900	8.866	64.332	58.604	5.155			
1000	8.909	65.268	59.224	6.044			
1045	8.925	65.657	59.489	6.446			
1045	8.925	65.657	59.489	6.446			
1100	8.944	66.119	59.813	6.937			
1200	8.974	66.899	60.372	7.832			
1300	9.001	67.618	60.902	8.731			
1400	9.027	68.286	61.406	9.633			
1500	9.052	68.910	61.886	10.537			
1600	9.077	69.495	62.343	11.443			
1641	9.088	69.722	62.522	11.816			
1641	9.088	69.722	62.522	11.816			
1700	9.103	70.046	62.780	12.352			
1800	9.131	70.568	63.199	13.264			
1900	9.162	71.062	63.600	14.178			
2000	9.195	71.533	63.985	15.096			
2100	9.231	71.983	64.356	16.017			
2200	9.270	72.414	64.713	16.942			
2300	9.312	72.827	65.057	17.871			
2400	9.357	73.225	65.389	18.805			
2500	9.405	73.608	65.711	19.743			
2600	9.455	73.978	66.022	20.686			
2690	9.503	74.301	66.294	21.539			
2690	9.503	74.301	66.294	21.539			
2700	9.508	74.337	66.324	21.634			
2800	9.564	74.684	66.617	22.588			
2900	9.621	75.021	66.902	23.547			
3000	9.681	75.349	67.179	24.512			
3100	9.742	75.668	67.448	25.483			
3200	9.804	75.979	67.711	26.460			
3300	9.868	76.283	67.967	27.443			
3400	9.933	76.579	68.216	28.433			
3500	9.999	76.869	68.461	29.430			
3600	10.066	77.153	68.699	30.433			
3700	10.134	77.430	68.932	31.442			
3800	10.202	77.703	69.161	32.459			
3900	10.272	77.970	69.385	33.482			
4000	10.341	78.232	69.604	34.513			
4100	10.412	78.490	69.819	35.550			
4200	10.483	78.743	70.030	36.594			
4300	10.554	78.992	70.237	37.645			
4400	10.626	79.237	70.440	38.704			
4500	10.699	79.478	70.640	39.769			
4600	10.771	79.715	70.837	40.842			
4700	10.844	79.950	71.030	41.922			
4800	10.918	80.180	71.220	43.009			
4900	10.991	80.408	71.408	44.103			
5000	11.065	80.633	71.592	45.205			
5100	11.139	80.855	71.774	46.314			
5200	11.214	81.074	71.953	47.430			
5300	11.288	81.291	72.129	48.554			
5400	11.363	81.505	72.304	49.685			
5500	11.437	81.716	72.475	50.824			
5600	11.512	81.925	72.645	51.970			
5700	11.586	82.132	72.813	53.123			
5800	11.661	82.337	72.978	54.284			
5900	11.736	82.540	73.142	55.452			
6000	11.810	82.741	73.303	56.627			

7. Titanium Borides

a. Titanium Diboride

The available data on the thermodynamics of titanium diboride have been reviewed, and work was started on the preparation of tables of thermodynamic functions.

The value of the heat of formation of TiB_2 has been subject to considerable uncertainty. The following values which range from -72 to -32 Kcal/mole have been reported:

Reference	ΔH°_{f298} (Kcal/mole)
Brewer and Haraldsen[440]	-72
Samsonov[441, 442]	-70
Schissel and Williams[120]	-32
Williams[443]	~ -50

Studies of the heat capacity had also been made, and reports containing C_p° data in the temperature range from 300° to 1200°K were available. However, additional data were necessary at high temperatures, and determinations were instituted in Phase III of this project. The latter work is discussed in section V-B.

Investigators	Temperature Range (°K) for Available C_p° Data
Margrave, et al[444]	420-1180
Krestovnikov and Vendrikh[445]	300-1000
Walker, Ewing, and Miller[446]	303-977
Ihnat (section V-B of this report)	Up to 2400
Pears, et al[447]	Up to destruction temperature

[440] Brewer, L. and H. Haraldsen, J. Electrochem. Soc. 102, 399 (1955).

[441] Samsonov, G.V., Zhur. Fiz. Khim. 30, 2059 (1956).

[442] Samsonov, G.V., Zhur. Prik. Khim. 28, 1018 (1955).

[443] Williams, W.S., Private Communication from P. Schissel.

[444] Margrave, J., D. Barnes, R. Mezaki, and R. Rutherford, Private Communication from J. Margrave.

[445] Krestovnikov, A.N. and M.S. Vendrikh, Thermodynamics of Titanium Diboride, Izv. Tsvet. Metall. 2, 54 (1959); Henry Brutcher Transl. No. 4673.

[446] Walker, B., C. Ewing, and R. Miller, J. Phys. Chem. 61, 1682 (1957).

[447] Pears, C.D. and S. Oglesby, The Thermophysical Properties of Refractory Materials from 2000°F to Their Destruction Temperatures, Southern Research Inst. Quart. Rept. 2, for WADD AF33(616)-7319 (November 1960).

Final calculations of thermodynamic functions were postponed temporarily until more high-temperature heat capacity data become available because of uncertainties encountered in extrapolating existing data to high temperatures. It was also considered worthwhile to review carefully the literature that has been uncovered for other thermochemical data that might be used in obtaining a better estimate of the heat of formation.

b. Other Borides (Ti_2B, TiB, and Ti_2B_5)

1) Physical property and structural data

In the Ti–B system there are several phases of somewhat lower stability than TiB_2 which are known. Hansen and Anderko[213] have given much of the basic physical property and structural data on these compounds.

a) Ti_2B

The compound Ti_2B was reported to have a tetragonal structure. Its temperature range of stability was in some doubt but was considered to be in the range from 1800° to 2200°C.

b) TiB

Conflicting data existed for the crystal structure of TiB. The reported structures were a cubic structure of the zinc blende type, a cubic structure of the NaCl type, and an orthorhombic structure of the FeB type. The compound has been considered to be stable from room temperature up to ~ 2060°C.

c) Ti_2B_5

Ti_2B_5 is reported to be hexagonal with a structure isotypic with that of W_2B_5. No actual melting point data have been presented for this compound, but the melting point appears to be lower than that of TiB_2.

2) Thermodynamic data

Brewer and Haraldsen[440] have discussed the titanium boride compounds and set limits for their heats of formation. However, there were insufficient data available in general for thermodynamic function calculations to be undertaken.

8. Titanium Carbide (TiC)

Titanium carbide has long been used as a tool material because of its characteristic hardness. Its high-temperature stability and its low density have made it very useful for many high-temperature applications. Typical uses have been discussed by Schwarzkopf and Kieffer.[448]

There have been several recent thermodynamic property compilations which included tables of data[75, 449, 450] for titanium carbide. However, experimental data have been reported since then which could affect these tables markedly. For example, Fujishiro and Gokcen[451] have reported vaporization experiments yielding a heat of formation for TiC of $\Delta H^\circ_{f298} = -31,333$ cal/gfw, whereas the earlier combustion experiments of Humphrey[452] (used in the aforementioned tabulations) yielded a value of $\Delta H^\circ_{f298} = -43,800$ cal/gfw.

The heat of formation of TiC is of considerable interest because of its usefulness in checking the heat of sublimation of Ti, which is uncertain, and because it can be used to evaluate the data of other refractories such as the titanium borides. It was therefore felt that a particularly careful evaluation of the heat of formation of TiC should be made. This evaluation was not complete at the time of report writing. Therefore, it was only possible to include the partial summary presented below.

a. Heat of Formation

1) Direct determinations

Fujishiro and Gokcen's[451] and Humphrey's[452] heats of formation of TiC given above appeared to be the only directly measured values reported.

2) Equilibrium data based on the reduction of TiO_2

The older work of Brantley and Beckman[453] has been often referred to as a source of thermochemical data for TiC. Those authors

[448] Schwarzkopf, P. and R. Kieffer, Refractory Hard Metals, Macmillan, N.Y. (1953).

[449] Beckett, C.W. et al, Preliminary Report on the Thermodynamic Properties of Selected Light Element Compounds, Nat. Bur. Stds. Rept. 6928 (1 July 1960).

[450] Elliott, J.F. and M. Gleiser, Thermochemistry for Steel-making, vol. I., Addison-Wesley, Reading, Mass. (1960).

[451] Fujishiro, S. and N. Gokcen, J. Phys. Chem. 65, 161 (1961).

[452] Humphrey, G.L., J. Am. Chem. Soc. 73, 2261 (1951).

[453] Brantley, L.R. and A.O. Beckman, J. Am. Chem. Soc. 52, 3956 (1930).

determined the equilibrium pressure of CO in a system which initially contained TiO_2 and C at temperatures from 1278° to 1428°K. They felt that reaction (231) was the one occurring.

$$TiO_2 + 3C \leftrightharpoons TiC + 2CO \quad (231)$$

Richardson[454] attempted to interpret their data but found it to yield free energies of formation equal to -64, 500 cal/gfw at 1200° K and -54, 480 cal/gfw at 1400° K. He concluded that their data must be in error or needed to be interpreted differently.

A more specific criticism of the Brantley and Beckman[453] work was made by Meerson and Krein[455] who stated that reaction (232) should be the final step.

$$TiO + 2C \leftrightharpoons TiC + CO \quad (232)$$

Furthermore, they pointed out that TiO and TiC form a continuous series of solid solutions.

Kutsev and Ormont[456] also conclude from high-temperature reduction studies in the range from 1880° to 2600°K that TiC and TiO form solid solutions. They stated that only three phases exist at equilibrium (i. e., TiC_xO_y , C, and CO) at the temperatures and pressures of their experiments although they suggested that the existence of a fourth-phase (Ti_2O_3) might be possible at lower temperatures.

Because Brantley and Beckman[453] claimed to have identified TiO_2 in their equilibrium mixture, their paper was carefully reviewed. X-ray diagrams were reproduced in their figure 5. From an examination of this figure, it appeared that the observed lines could be ascribed to TiC and graphite and the existence of TiO_2 in their mixture seemed to be seriously in doubt. Brantley and Beckman's[453] results were therefore interpreted here as pertaining to the TiC_xO_y-C-CO system for which the equilibrium is given by reaction (233).

$$TiO_{(soln)} + C_{(s)} \leftrightharpoons TiC_{(soln)} + CO_{(g)} \quad (233)$$

[454] Richardson, F.D., J. Iron Steel Inst. 175, 33 (1953).

[455] Meerson, G.A. and O.E. Krein, Russian J. Appl. Chem. 25, 143 (1952).

[456] Kutsev, V.S. and B.F. Ormont, Zhur. Fiz. Khim. 31, 1866 (1957).

Further thermodynamic calculations were not possible because concentrations or activities of the TiO and TiC in solution were not reported.

The results of Meerson and Krein[455] and Kutsev and Ormont[456] for the Ti-C-O system were being studied in more detail at the time of report writing to determine whether they could be used as a source of thermodynamic data.

3) Equilibrium data in the Ti-Ta-C system

Since the TiC and TaC compounds have approximately the same thermodynamic stabilities, a search of the literature was made for more specific data on the Ti-Ta-C system. The work of McMullin and Norton[457] yielded an isothermal section of the ternary diagram at 1820°C. They found that three phases (β-γ-δ) coexisted in equilibrium. These phases had the following compositions in atomic percent:

Phase	Atomic percent Ta	Atomic percent Ti	Atomic percent C
β	60	38	2
γ	67	0	33
δ	22	50	28

The β-phase is essentially a solid solution of Ta and Ti; the γ-phase is essentially Ta_2C; and the δ-phase is a solid solution of TiC-TaC. The equilibrium involved can be represented by reaction (234).

$$2Ta_{(\beta)} + TiC_{(\delta)} \rightleftharpoons Ta_2C_{(\gamma)} + Ti_{(\beta)} \quad . \tag{234}$$

The following activities were calculated from Raoult's law applied to the components in high concentration in the solid solutions:

457 McMullin, J.G. and J.T. Norton, J. Metals 5, 1205 (1953).

Phase	Composition	a_{Ta}	a_{Ti}	a_{Ta_2C}	a_{TiC}
β	$Ta_{0.60}Ti_{0.38}C_{0.02}$	0.60	0.38	---	---
γ	$Ta_{0.67}C_{0.33}$	---	---	1	---
δ	$(TiC)_{0.28}Ti_{0.22}Ta_{0.22}$ or $(TiC)_{0.388}Ti_{0.305}Ta_{0.305}$	---	---	---	0.388

The equilibrium constant in equation (235),

$$K = \frac{a_{Ta_2C}\,a_{Ti}}{a_{TiC}\,a_{Ta}^2} \quad , \qquad (235)$$

is therefore equal to 2.77, and the standard free-energy change for reaction (234) is -4232 cal/gfw when calculated from equation (191).

Since equation (236) holds for reaction (234),

$$\Delta F^\circ = \Delta F^\circ_{Ti} + \Delta F^\circ_{Ta_2C} - \Delta F^\circ_{TiC} - 2\Delta F^\circ_{Ta} \quad , \qquad (236)$$

and the free energies in the standard state are zero for the elements, equation (237) obtains.

$$\Delta F^\circ = \Delta F^\circ_{Ta_2C} - \Delta F^\circ_{TiC} \quad . \qquad (237)$$

Since Elliott and Gleiser[450] have reported that $\Delta F^\circ_{Ta_2C,\,2093^\circ K} =$ -31,200 cal/mole, it was possible to calculate that $\Delta F^\circ_{TiC,\,2093^\circ K} =$ -26,968 cal/mole from equation (237). With the free-energy functions from the JANAF tables,[75] it was then found that $\Delta H^\circ_{298,\,TiC} =$ -33,768 cal/mole.

The above analysis therefore gave a ΔH°_{298} value in good agreement with that of Fujishiro and Gokcen[451] of ΔH°_{298} = -31,333. This provides evidence in support of the validity of their data rather than the heat-of-combustion data of Humphrey.[452] (At this stage, too much emphasis should not be placed on this analysis since further work is planned.)

The principal source of uncertainty in the latter analysis is the application of Raoult's law to the solid solutions. An analysis of the work in the Ti–C–O system by Kutsev and Ormont[456] may make possible an independent check of these results.

b. Condensed Phase Data

1) Crystalline forms

TiC has a face-centered cubic structure of the NaCl type.[213] The lattice parameter for the stoichiometric composition is a = 4.329 ± 0.001 Å.

2) Phase-transformation temperatures

a) Melting Point

Several reported melting points have been reviewed by Hansen and Anderko.[213]

m.p. (°C)	Reference
3160	Friederich and Sittig[458]
3140	Agte and Moers[459]
3030	Geach and Jones[460]
3250	Schwartzkopf and Kieffer[448]

The average of these determinations is 3145°C (3418°K), and is in good agreement with the value (3410°K) used by the Bureau of Standards[449] and the JANAF tables.[75] The latter value was adopted and an estimated uncertainty of ± 100°K was assigned to it.

b) Boiling point

There were few published data regarding the boiling point of TiC. The National Research Council tables[461] listed a value

[458] Friederich, E. and L. Sittig, Z. anorg. Chem. 144, 171 (1925).

[459] Agte, C. and K. Moers, Z. anorg. Chem. 198, 233 (1931).

[460] Geach, G.A. and F.O. Jones, Plansee Proc. p. 80 (1955).

[461] Silverman, A., Data on Chemicals for Ceramic Use, Nat. Research Council Bull. 118 (June 1949).

of 4300°C (4573°K) but did not give an original reference. On the basis of the work of Fujishiro and Gokcen[451] and of Chupka, Berkowitz, Giese, and Inghram,[462] who showed that the primary vaporization products are the elemental species, it should be possible to calculate the temperature at which the decomposition pressure reaches one atmosphere.

3) Heat changes

a) Heat of fusion

Reports of experimental determinations of the heat of fusion of TiC were not found. Experimental measurements would be rather difficult to make because of the very high melting point of this compound. An NBS report[331] gave an estimate of this quantity obtained on the assumption of an entropy of fusion of 2.5 e.u./g atom or 5 e.u./mole of TiC. On this basis, the heat of fusion was thus calculated to be 17,050 cal/mole. The latter value has been used in both the NBS[449] and JANAF tables[75] and was accepted here.

b) Heat of vaporization

Calculations of the heat of sublimation or vaporization can be made if the heat of formation of the compound is known together with the heats of sublimation of the elemental species. On the assumption that TiC dissociates into atoms (e.g., species such as C_2, C_3 are neglected) and that $\Delta H^\circ_{f,\,TiC,\,298} = -43.8$ Kcal/mole, NBS workers found a value of $\Delta H^b_{sublimation,\ 298°K} =$ 328.51 Kcal/mole. It is expected that this value will be lowered somewhat by the acceptance of a more positive value of the heat of formation.

4) Heat capacity

a) Low-temperature data

Experimental heat capacity data by Kelley[463] for the temperature range from 55° to 295°K have been analyzed by the NBS[331] who found that $S^\circ_{298} = 5.80 \pm 0.10$ e.u. This value was adopted for the present tabulation.

[462]Chupka, W.A., J. Berkowitz, C.F. Giese, and M.G. Inghram, J. Phys. Chem. 62, 611 (1958).

[463]Kelley, K.K., Ind. Eng. Chem. 36, 865 (1944).

b) High-temperature data

The heat capacity data of Naylor[464] in cal/°K gfw over the temperature range from 298° to 1735°K have been reviewed and accepted by Kelley[56] who gave equation (238)

$$C_p^\circ = 11.83 + 0.80 \times 10^{-3}T - 3.58 \times 10^{5}T^{-2} \qquad (238)$$

for the temperature range from 298° to 2000°K. C_p° data obtained on the present project are discussed in section V-B below and compared with data from other sources.

c) Liquid heat capacity

The heat capacity of liquid TiC was reported by the NBS[331] to be the estimated value of 7.8 cal/g atom °K (15.6 cal/mole °K) at the melting point. It was felt here that their further assumption of a negative temperature coefficient was not sufficiently justified, and that a better choice will be possible when better data on the solid become available.

[464] Naylor, B.F., J. Am. Chem. Soc. 68, 370 (1946).

9. Titanium Oxides (TiO, Ti_2O_3, Ti_3O_5, and TiO_2)

The Ti-O system is relatively complicated as indicated by its phase diagram.[213] The known oxides of titanium for which data were available are TiO, Ti_2O_3, Ti_3O_5, and TiO_2. A δ-phase of approximately Ti_4O_3 composition in the system had been reported, but its existence had not been established with certainty. The literature on the first four above-listed compounds was reviewed, and the data were under analysis at the time of report writing. Complete tables of thermodynamic function were under preparation for all solid phases.

10. Tungsten Oxides

The important oxides of tungsten for which thermodynamic properties have been compiled are tungsten monoxide (WO), tungsten dioxide (WO_2), and tungsten trioxide (WO_3). Although polymeric species of WO_3; i.e., $(WO_3)_3$, $(WO_3)_4$, etc., are known to exist, virtually no thermodynamic data were available on them. Estimation of the thermodynamic properties of these polymeric species was not attempted.

a. Tungsten Monoxide (WO)

Tungsten monoxide does not appear to exist in a pure condensed phase, but may be part of the solid oxide layer formed during surface oxidation of tungsten metal.[264] The existence of WO in the gas phase at high temperatures has been verified by mass spectrographic work.[410] Only the thermodynamic functions for gaseous WO are given in the present compilation. The thermodynamic functions for gaseous WO given in Table LXIX were calculated by means of the computer program described in section III-F with the following estimated molecular data:

Bond distance

$$r_o = 1.78 \text{Å} .$$

Moment of inertia

$$I = 77.426 \times 10^{-40} \text{ g cm}^2 .$$

Symmetry number

$$\theta = 1 .$$

Fundamental frequency

$$\omega = 803 \text{ cm}^{-1} .$$

Ground electronic state

$$^1\Sigma$$

1) Bond distance

The W-O bond distance had not been experimentally determined. A value of 1.70Å had been calculated[410] by means of the Guggenheimer relation[465] and the estimated fundamental frequency of Vittalachar

[465]Guggenheimer, K. M., Proc. Phys. Soc. (London) 58, 456 (1946).

TABLE LXIX

TUNGSTEN MONOXIDE — IDEAL MOLECULAR GAS — OW

Reference State for Calculating ΔH_f°, ΔF_f°, and $\text{Log } K_p$: Solid W from 298.15° to 3650°K, Liquid W from 3650° to 5891°K, Gaseous W from 5891° to 6000°K; Gaseous O_2; Gaseous WO.

gfw = 199.86

T, °K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal gfw)	ΔH_f° (Kcal gfw)	ΔF_f° (Kcal gfw)	Log K_p
0	0.000	0.000	Infinite	-2.122	97.510	97.510	Infinite
298.15	7.601	56.597	56.597	0.000	97.400	90.166	-66.090
300	7.609	56.643	56.597	0.014	97.396	90.121	-65.650
400	7.990	58.888	56.900	0.795	97.234	87.730	-47.931
500	8.252	60.701	57.485	1.608	97.081	85.362	-37.310
600	8.428	62.222	58.151	2.443	96.931	83.044	-30.247
700	8.547	63.531	58.828	3.292	96.777	80.728	-25.203
800	8.631	64.678	59.489	4.151	96.616	78.461	-21.433
900	8.691	65.698	60.123	5.017	96.446	76.184	-18.499
1000	8.736	66.616	60.728	5.889	96.273	73.962	-16.164
1100	8.770	67.450	61.301	6.764	96.088	71.717	-14.248
1200	8.796	68.215	61.846	7.642	95.896	69.535	-12.663
1300	8.817	68.920	62.363	8.523	95.689	67.319	-11.317
1400	8.834	69.574	62.855	9.405	95.466	65.145	-10.169
1500	8.847	70.183	63.324	10.290	95.230	62.988	-9.177
1600	8.859	70.755	63.771	11.175	94.973	60.843	-8.310
1700	8.868	71.292	64.197	12.061	94.701	58.721	-7.549
1800	8.876	71.799	64.606	12.948	94.410	56.614	-6.873
1900	8.883	72.279	64.997	13.836	94.104	54.521	-6.271
2000	8.888	72.735	65.373	14.725	93.780	52.444	-5.731
2100	8.893	73.169	65.734	15.614	93.439	50.387	-5.244
2200	8.898	73.583	66.081	16.503	93.080	48.345	-4.802
2300	8.901	73.978	66.416	17.393	92.705	46.320	-4.401
2400	8.905	74.357	66.739	18.284	92.311	44.314	-4.035
2500	8.908	74.721	67.051	19.174	91.900	42.323	-3.700
2600	8.910	75.070	67.353	20.065	91.472	40.347	-3.391
2700	8.913	75.407	67.645	20.956	91.028	38.386	-3.107
2800	8.915	75.731	67.928	21.848	90.565	36.445	-2.845
2900	8.917	76.044	68.202	22.739	90.085	34.525	-2.602
3000	8.918	76.346	68.469	23.631	89.588	32.613	-2.376
3100	8.920	76.638	68.728	24.523	89.075	30.724	-2.166
3200	8.921	76.922	68.979	25.415	88.543	28.854	-1.971
3300	8.922	77.196	69.224	26.307	87.995	26.994	-1.788
3400	8.924	77.463	69.463	27.200	87.431	25.153	-1.617
3500	8.925	77.721	69.695	28.092	86.848	23.328	-1.457
3600	8.926	77.973	69.921	28.985	86.249	21.528	-1.307
3650	8.927	78.095	70.032	29.431	85.944	20.633	-1.235
3650	8.927	78.095	70.032	29.431	77.549	20.633	-1.235
3700	8.927	78.217	70.142	29.877	77.250	19.851	-1.172
3800	8.927	78.455	70.358	30.770	76.650	18.312	-1.053
3900	8.928	78.687	70.569	31.663	76.049	16.774	-0.940
4000	8.929	78.913	70.774	32.555	75.445	15.276	-0.835
4100	8.930	79.134	70.976	33.448	74.840	13.768	-0.734
4200	8.930	79.349	71.172	34.341	74.233	12.247	-0.637
4300	8.931	79.559	71.365	35.234	73.624	10.827	-0.550
4400	8.931	79.764	71.554	36.128	73.014	9.372	-0.465
4500	8.932	79.965	71.738	37.021	72.402	7.929	-0.385
4600	8.932	80.161	71.919	37.914	71.787	6.509	-0.309
4700	8.933	80.353	72.097	38.807	71.169	5.095	-0.237
4800	8.933	80.542	72.271	39.700	70.549	3.691	-0.168
4900	8.933	80.726	72.441	40.594	69.926	2.313	-0.103
5000	8.934	80.906	72.609	41.487	69.299	0.940	-0.041
5100	8.934	81.083	72.773	42.381	68.668	-0.423	0.018
5200	8.935	81.257	72.935	43.274	68.031	-1.768	0.074
5300	8.935	81.427	73.093	44.167	67.387	-3.101	0.128
5400	8.935	81.594	73.249	45.061	66.737	-4.417	0.179
5500	8.935	81.758	73.402	45.954	66.078	-5.731	0.228
5600	8.936	81.919	73.553	46.848	65.408	-7.034	0.274
5700	8.936	82.077	73.701	47.742	64.726	-8.322	0.319
5800	8.936	82.232	73.847	48.635	64.027	-9.593	0.361
5891	8.936	82.371	73.977	49.449	63.376	-10.739	0.398
5891	8.936	82.371	73.977	49.449	-128.889	-10.739	0.398
5900	8.936	82.385	73.990	49.529	-128.951	-10.567	0.391
6000	8.937	82.535	74.132	50.422	-129.663	-8.550	0.311

and Krishnamurty.[466] A value of 1.78Å had been estimated for this distance by Brewer and Chandrasekharaiah.[401] The value 1.78Å was chosen for the present work.

2) Moment of inertia

The moment of inertia, I, was calculated from the assumed value for the W-O bond distance by means of equation (239)

$$I = \frac{M_W M_O}{M_W + M_O} r_o^2 \quad , \qquad (239)$$

where

M_W = mass of tungsten atom

M_O = mass of oxygen atom

r_o = W-O bond distance.

3) Fundamental frequency

The fundamental frequency ω, of WO had not been experimentally determined. An approximate band analysis by Vittalachar and Krishnamurty[466] was the basis for a suggested value of 1060 cm^{-1}. This same value was also used in a paper by Gatterer and Krishnamurty.[467] However, the 1060 cm^{-1} value was estimated from a comparison with other transition monoxides, and the value employed for a key item in the comparison (i.e., ω for TaO) was incorrect.[468] Brewer and Chandrasekharaiah[401] estimated the fundamental frequency to be 803 cm^{-1}. The 803 cm^{-1} value was chosen in the present work as being more in accord with the postulate that the bonding in CrO, MoO, and WO are very similar. Mass effects alone would therefore indicate a frequency order of $\omega_{Cr} > \omega_{Mo} > \omega_W$. In view of the large uncertainty associated with the value of ω, no attempt was made to include anharmonicity and interaction terms in the calculation of thermodynamic functions for the WO molecule.

4) Electronic states

The electronic states of WO were unknown. As in the similar case of MoO, only the ground state was included; and it was assumed to be a $^1\Sigma$ state.

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[466] Vittalachar, V. and S. G. Krishnamurty, Current Sci. 23, 357 (1954).

[467] Gatterer, A. and S. G. Krishnamurty, Nature 169, 543 (1952).

[468] Premaswarup, D. and R. F. Barrow, Nature 180, 602 (1957).

The standard enthalpy of formation, $\Delta H^o_{f\,298}$, had not been directly determined. The value of ΔH^o_{f298} was, therefore, determined by an indirect method identical to that employed in the case of MoO described in section IV-B5a of this report. The required partial pressures of WO and monatomic oxygen in equilibrium with solid tungsten were those measured by DeMaria and co-workers[410] in their mass spectrographic study of Al_2O_3 in tungsten containers. The value of the heat of formation so obtained was + 97, 400 $\pm$ 4500 cal/gfw. $H^o_{298}-H_0$ for gaseous WO was found to be 2122 cal/gfw.

Values of ΔH^o_f, ΔF^o_f, and $\log_{10} K_p$ were calculated in a fashion identical to that described in section IV-B5a for the corresponding MoO molecule.

b. Tungsten Dioxide (WO_2)

1) Condensed phase

The thermodynamic properties of solid WO_2 have been based on the low-temperature heat capacity data of King, Weller, and Christensen,[415] the high-temperature enthalpy data of the same workers, and the heat-of-formation data of Mah.[469]

The only experimental investigation of the low-temperature heat capacity of WO_2 has been that of King, Weller, and Christensen[415] who made measurements over the temperature range from 52° to 297°K. Their data yield an S^o_{298} value of 12.08 $\pm$ 0.07 e.u./gfw.

The only experimental high-temperature enthalpy data were those of King, Weller, and Christensen[415] (400° to 1800°K). The smoothed values reported by these workers were employed in the present compilation, except that those near room temperature were altered slightly to join the low-temperature data smoothly at 298.15°K. Tabular entropy values were calculated by the procedure of Kelley.[56] The free-energy functions in Table LXX were calculated from equation (108). Heat capacity values were calculated from equation (240)

$$C^o_p = 15.49 + 3.58 \times 10^{-3}T - 2.80 \times 10^5 T^{-2} \qquad (240)$$

except for the values calculated near room temperature which were altered slightly to join the low-temperature data smoothly at 298.15°K.

[469] Mah, A. D., J. Am. Chem. Soc. 81, 1582 (1959).

TABLE LXX

TUNGSTEN DIOXIDE — CONDENSED PHASE — O_2W

Reference State for Calculating ΔH_f°, ΔF_f°, and Log K_p :
Solid W; Gaseous O_2; Solid WO_2.

gfw = 215.86

T, °K	C_p° (cal/°K gfw)	S_T° (cal/°K gfw)	$-(F_T^\circ - H_{298}^\circ)/T$ (cal/°K gfw)	$H_T^\circ - H_{298}^\circ$ (Kcal/gfw)	ΔH_f° (Kcal/gfw)	ΔF_f° (Kcal/gfw)	Log K_p
0	0.000	0.000	Infinite	-2.077	-139.747	-139.747	Infinite
298.15	13.320	12.080	12.080	0.000	-140.940	-127.596	93.526
300	13.350	12.162	12.080	0.025	-140.939	-127.513	92.889
400	15.172	16.266	12.618	1.459	-140.803	-123.041	67.223
500	16.160	19.767	13.707	3.030	-140.564	-118.636	51.853
600	16.860	22.827	14.994	4.700	-140.257	-114.277	41.623
700	17.425	25.493	16.293	6.440	-139.908	-109.977	34.335
800	17.916	27.884	17.596	8.230	-139.538	-105.713	28.878
900	18.366	30.026	18.859	10.050	-139.160	-101.524	24.652
1000	18.790	31.975	20.075	11.900	- 38.770	-97.342	21.273
1100	19.197	33.767	21.240	13.780	-138.369	-93.242	18.524
1200	19.592	35.419	22.352	15.680	-137.963	-89.130	16.232
1300	19.978	36.965	23.419	17.610	-137.549	-85.107	14.307
1400	20.359	38.417	24.438	19.570	-137.126	-81.091	12.658
1500	20.736	39.804	25.417	21.580	-136.673	-77.103	11.233
1600	21.109	41.147	26.359	23.660	-136.173	-73.150	9.991
1700	21.479	42.468	27.268	25.840	-135.593	-69.231	8.900
1800	21.847	43.771	28.149	28.120	-134.935	-65.345	7.934
1900	22.214	45.058	29.005	30.500	-134.196	-61.499	7.074
2000	22.580	46.330	29.840	32.980	-133.379	-57.692	6.304

WO_2 does not exhibit a true melting point since disproportionation occurs to yield solid W and WO_3 vapor (probably including WO_3 polymeric species) before melting occurs.[470, 346]

The standard enthalpy of formation, ΔH°_{f298}, of solid WO_2 was determined by Mah[469] from the heats of combustion of $W_{(s)}$ to $WO_{3(s)}$ and of $WO_{2(s)}$ to $WO_{3(s)}$. Mah's[469] value of -140, 940 $\pm$ 210 cal/gfw was accepted in the present compilation. Other less accurate values have been reported by Delepine and Hallopeau,[471] by Coughlin,[472] and by Griffis.[473, 474]

Values of ΔH°_f, ΔF°_f, and $\log_{10}K_P$ were calculated from equations (44), (241), and (242).

$$\Delta H^\circ_f = \Delta H^\circ_{f298} + (H^\circ_T - H^\circ_{298})_{WO_{2(s)}} - (H^\circ_T - H^\circ_{298})_{W_{(s)}} - (H^\circ_T - H^\circ_{298})_{O_{2(g)}} \quad (241)$$

$$\Delta F^\circ_f = \Delta H^\circ_{f298} + (F^\circ_T - H^\circ_{298})_{WO_{2(s)}} - (F^\circ_T - H^\circ_{298})_{W_{(s)}} - (F^\circ_T - H^\circ_{298})_{O_{2(g)}} . \quad (242)$$

2) Ideal gas

All of the molecular constants required in the calculation of the thermodynamic functions for gaseous WO_2 have been estimated since no experimental spectroscopic data have been reported. The thermodynamic functions for gaseous WO_2 given in Table LXXI were calculated by means of the machine program described in section III-F with the following molecular data:

Molecular configuration

Symmetrical, nonlinear molecule with

$\angle$ O–W–O = 107 deg

r_o = 1.78 Å .

Product of moments of inertia

$I_AI_BI_C = 880082 \times 10^{-120} g^3 cm^6$.

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[470] Brewer, L., Chem. Revs. 52, 1 (1953).

[471] Delepine, M. and L.A. Hallopeau, Compt. rend. 131, 186 (1900).

[472] Coughlin, J.P., U.S. Bur. Mines Bull. 542 (1954).

[473] Griffis, R.C., J. Electrochem. Soc. 106, 418 (1959).

[474] Griffis, R.C., J. Electrochem. Soc. 105, 398 (1958).

TABLE LXXI

TUNGSTEN DIOXIDE — IDEAL MOLECULAR GAS — O_2W

Reference State for Calculating ΔH_f°, ΔF_f°, and $\text{Log } K_p$: Solid W from 298.15° to 3650°K, Liquid W from 3650° to 5891°K, Gaseous W from 5891° to 6000°K; Gaseous O_2; Gaseous WO_2.

gfw = 215.86

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-2.693	14.477	14.477	Infinite
298.15	10.814	65.893	65.893	0.000	13.900	11.200	-8.209
300	10.835	65.960	65.893	0.020	13.896	11.183	-8.146
400	11.762	69.213	66.330	1.153	13.731	10.314	-5.635
500	12.370	71.908	67.184	2.362	13.608	9.466	-4.019
600	12.767	74.201	68.167	3.620	13.503	8.659	-3.154
700	13.035	76.190	69.174	4.911	13.403	7.846	-2.450
800	13.222	77.944	70.163	6.224	13.296	7.074	-1.932
900	13.356	79.509	71.116	7.554	13.184	6.285	-1.526
1000	13.455	80.922	72.027	8.894	13.064	5.546	-1.212
1100	13.530	82.208	72.895	10.244	12.935	4.777	-0.949
1200	13.588	83.388	73.721	11.600	12.797	4.067	-0.741
1300	13.634	84.477	74.507	12.961	12.642	3.318	-0.558
1400	13.671	85.489	75.256	14.326	12.470	2.605	-0.407
1500	13.701	86.433	75.970	15.695	12.282	1.908	-0.278
1600	13.726	87.318	76.652	17.066	12.073	1.222	-0.167
1700	13.747	88.151	77.304	18.440	11.847	0.551	-0.071
1800	13.764	88.937	77.929	19.816	11.601	-0.108	0.013
1900	13.779	89.682	78.528	21.193	11.337	-0.751	0.086
2000	13.792	90.389	79.103	22.571	11.052	-1.378	0.151
2100	13.803	91.062	79.657	23.951	10.749	-1.991	0.207
2200	13.812	91.704	80.190	25.332	10.426	-2.592	0.257
2300	13.820	92.319	80.704	26.713	10.084	-3.176	0.302
2400	13.828	92.907	81.200	28.096	9.722	-3.744	0.341
2500	13.834	93.472	81.680	29.479	9.340	-4.298	0.376
2600	13.840	94.014	82.144	30.863	8.939	-4.836	0.406
2700	13.845	94.537	82.593	32.247	8.518	-5.357	0.434
2800	13.850	95.040	83.029	33.632	8.078	-5.863	0.458
2900	13.854	95.526	83.452	35.017	7.618	-6.354	0.479
3000	13.857	95.996	83.862	36.402	7.138	-6.828	0.497
3100	13.861	96.450	84.261	37.788	6.640	-7.282	0.513
3200	13.864	96.891	84.649	39.175	6.122	-7.725	0.528
3300	13.867	97.317	85.029	40.561	5.586	-8.158	0.540
3400	13.869	97.731	85.394	41.948	5.030	-8.558	0.550
3500	13.871	98.133	85.752	43.335	4.456	-8.946	0.559
3600	13.874	98.524	86.101	44.722	3.862	-9.317	0.566
3650	13.875	98.714	86.272	45.416	3.559	-9.497	0.569
3650	13.875	98.714	86.272	45.416	-4.836	-9.497	0.569
3700	13.876	98.904	86.442	46.110	-5.132	-9.561	0.565
3800	13.877	99.274	86.775	47.497	-5.730	-9.671	0.556
3900	13.879	99.635	87.100	48.885	-6.331	-9.770	0.547
4000	13.881	99.986	87.418	50.273	-6.935	-9.844	0.538
4100	13.882	100.329	87.729	51.661	-7.543	-9.918	0.529
4200	13.883	100.664	88.033	53.049	-8.155	-9.962	0.518
4300	13.885	100.990	88.330	54.438	-8.769	-9.989	0.508
4400	13.886	101.309	88.622	55.826	-9.389	-10.014	0.497
4500	13.887	101.622	88.907	57.215	-10.011	-10.026	0.487
4600	13.888	101.927	89.187	58.604	-10.638	-10.014	0.476
4700	13.889	102.225	89.461	59.993	-11.270	-9.992	0.465
4800	13.890	102.518	89.730	61.382	-11.908	-9.955	0.453
4900	13.891	102.804	89.994	62.771	-12.552	-9.908	0.442
5000	13.891	103.085	90.253	64.160	-13.204	-9.845	0.430
5100	13.892	103.360	90.507	65.549	-13.865	-9.772	0.419
5200	13.893	103.630	90.757	66.938	-14.536	-9.682	0.407
5300	13.894	103.894	91.002	68.327	-15.220	-9.577	0.395
5400	13.894	104.154	91.244	69.717	-15.918	-9.466	0.383
5500	13.895	104.409	91.481	71.106	-16.634	-9.339	0.371
5600	13.895	104.659	91.714	72.496	-17.371	-9.201	0.359
5700	13.896	104.905	91.943	73.885	-18.134	-9.040	0.347
5800	13.896	105.147	92.169	75.275	-18.928	-8.874	0.334
5891	13.897	105.364	92.371	76.540	-19.684	-8.701	0.323
5891	13.897	105.364	92.371	76.540	-211.949	-8.701	0.323
5900	13.897	105.385	92.391	76.665	-212.021	-8.396	0.311
6000	13.897	105.618	92.609	78.054	-212.869	-4.926	0.179

Symmetry number

$\theta = 2$

Fundamental frequencies

$\omega_1 = 794 \text{ cm}^{-1}$

$\omega_2 = 351 \text{ cm}^{-1}$

$\omega_3 = 812 \text{ cm}^{-1}$.

Ground electronic state

$^1\Sigma$

a) Molecular configuration

The molecular configuration of the WO_2 molecule was unknown. Consideration of the periodic group to which tungsten belongs and the work of Walsh[395] on bonding and structural relations led to the conclusion that WO_2 is a symmetric, nonlinear molecule, and it was so considered in the present work. DeMaria and co-workers[410] also assumed it to have a nonlinear structure, whereas Chandrasekharaiah and Brewer[397] assumed it to have the linear structure which they assumed for all of the Group IV, V, and VI transition metal dioxides. An O-W-O angle of 107 degrees was chosen in the present work as representing a reasonable value in comparison with known compounds of similar bonding. The W-O bond distance was assumed to be identical to the estimated corresponding distance for the tungsten monoxide (WO) molecule; i. e., 1.78A.

b) Moments of inertia

The moments of inertia of WO_2 were calculated in a manner analogous to that used for the corresponding CrO_2 molecule.

c) Fundamental frequencies

The fundamental frequencies of WO_2 were estimated by the same method used for the corresponding CrO_2 molecule (see section IV-B3a), except that the stretching force constant for WO was calculated from estimated spectroscopic data.[401] The frequencies so obtained are somewhat lower than those estimated by DeMaria and co-workers.[410]

d) Electronic states

The electronic states for WO_2 were treated in the same manner as those of the CrO_2 molecule (section IV-B3a).

The standard enthalpy of formation, ΔH°_{f298}, of gaseous WO_2 had not been directly determined. The value of ΔH°_{298} was, therefore, determined by an indirect method identical to that employed in the case of MoO_2 (see section IV-B5b) based on the mass spectrographic study of Al_2O_3 in tungsten containers by DeMaria and coworkers.[410] The value of ΔH°_{f298} so obtained was + 13, 900 $\pm$ 5000 cal/gfw. H°_{298}-H°_0 for gaseous WO_2 was found to be 2693 cal/gfw.

Values of ΔH°_f, ΔF°_f, and $\log_{10} K_P$ were calculated in an identical fashion to that described in section IV-B5b for the corresponding MoO_2 molecule.

c. Tungsten Trioxide (WO_3)

1) Condensed phase

a) The 1050°K transition

Tungsten trioxide is monoclinic at room temperature but undergoes a transition to the tetragonal form at 1050°K. A value of about 725°C for the transition temperature has been quoted,[346] but the recent work of King, Weller, and Christensen[415] has established 1050° $\pm$ 10°K as the best value. The heat of transition, from enthalpy measurements on the two forms,[415] was found to be 410 cal/gfw. An uncertainty of $\pm$ 40 cal/gfw has been arbitrarily assigned to the heat of transition.

b) Melting point and heat of fusion

The works of Jaeger and Germs[475] and of King and co-workers[415] are in excellent agreement on the melting point of 1745° $\pm$ 10°K for WO_3. The heat of fusion, as determined from enthalpy measurements,[415] is 17, 550 cal/gfw. An uncertainty of $\pm$ 1000 cal/gfw has been arbitrarily assigned to the heat of fusion.

[475] Jaeger, F.M. and H.C. Germs, Z. anorg. Chem. 119, 149 (1921).

c) Boiling point

The equilibrium vapor above WO_3 consists primarily of $(WO_3)_3$, $(WO_3)_4$, and $(WO_3)_5$ according to Berkowitz, Chupka, and Inghram.[476] Other investigations concerning the vapor pressure of WO_3 are those of Blackburn, Hoch, and Johnston,[417] and of Meyer, Oosterom and deRoo.[477] No attempt has been made in the present work to define a boiling point for WO_3. A temperature of about 2100°K has been quoted[470] as the temperature at which the total pressure above WO_3 becomes one atmosphere. No attempt was made to estimate thermodynamic functions for the polymeric vapor species.

d) Entropy at 298.15°K

Low-temperature heat capacity data for $WO_{3(s)}$ have been reported by King, Weller, and Christensen,[415] and by Seltz, Dunkerley, and DeWitt.[429] The results of Seltz and co-workers were appreciably higher than those of King and co-workers, and were believed to be subject to some systematic error.[415] The data of King and co-workers yielded an S°_{298} value of 18.15 ± 0.12 e.u.

e) Thermodynamic properties

The only experimental high-temperature enthalpy measurements on WO_3 are those of King, Weller, and Christensen[415] over the temperature range from 400° to 1840°K. Equation (243) for the heat capacity in cal/°K gfw, derived from their enthalpy data for the monoclinic form of WO_3,

$$C^\circ_p = 21.26 + 3.38 \times 10^{-3}T - 4.42 \times 10^5 T^{-2} , \qquad (243)$$

was used to calculate C°_p values from 400°K to the transition point (1050°K). These values were then extrapolated to join the low-temperature heat capacity data smoothly at 298.15°K. Enthalpy and entropy values in the range from 298.15° to 400°K were determined by graphical integration with these extrapolated heat capacity values. Enthalpy and entropy values in units of calories, °K, and moles were calculated at other temperatures up to the transition point from equations (244) and (245).

[476] Berkowitz, J., W.A. Chupka, and M.G. Inghram, J. Chem. Phys. 27, 85 (1957).

[477] Meyer, G., J.F. Oosterom, and J.L. deRoo, Rec. trav. chim. 78, 412 (1959).

$$H^\circ_T - H^\circ_{298} = 21.26T + 1.69 \times 10^{-3}T^2 + 4.42 \times 10^5 T^{-1} - 7962 \qquad (244)$$

$$S^\circ_T = 21.26 \ln T + 3.38 \times 10^{-3}T + 2.21 \times 10^5 T^{-2} - 106.448 \ . \qquad (245)$$

Free-energy functions for monoclinic WO_3 were calculated in the usual manner.

Heat capacities of tetragonal WO_3 in cal/°K gfw were calculated from the transition point (1050°K) to the melting point (1745°K) by means of equation (246) derived from the enthalpy data of King and co-workers.

$$C^\circ_p = 20.79 + 2.75 \times 10^{-3}T \ . \qquad (246)$$

Enthalpy and entropy values in units of calories, °K, and moles were calculated for tetragonal tungsten trioxide from equations (247) and (248).

$$H^\circ_T - H^\circ_{298} = 20.79T + 1.375 \times 10^{-3}T^2 - 6290 \qquad (247)$$

$$S^\circ_T = 20.79 \ln T + 2.75 \times 10^{-3}T - 101.928 \ . \qquad (248)$$

Free-energy functions were calculated from the enthalpy and entropy values in the usual manner.

The heat capacity of liquid WO_3 was found to be 31.50 cal/°K gfw;[415] hence, enthalpy and entropy values in units of calories, °K, and moles were obtained from equations (249) and (250).

$$H^\circ_T - H^\circ_{298} = 31.50\,T - 3242 \qquad (249)$$

$$S^\circ_T = 31.50 \ln T - 167.017 \ . \qquad (250)$$

The thermodynamic functions of the condensed phases of WO_3 are summarized in Table LXXII.

f) Standard heat of formation at 298.15°K ($\Delta H^\circ_{f\,298}$)

The standard enthalpy of formation, $\Delta H^\circ_{f\,298}$, of solid WO_3 was determined by Mah[469] from the heat of combustion of tungsten metal. Mah's value of -201,460 ± 200 cal/gfw was accepted

TABLE LXXII

TUNGSTEN TRIOXIDE — **CONDENSED PHASES** — O_3W

Reference State for Calculating ΔH_f°, ΔF_f°, and Log K_p : Solid W; Gaseous O_2, Solid WO_3 from 298.15° to 1745°K, Liquid WO_3 from 1745° to 2000°K.

gfw = 231.86 — $T_t(I)$ = 1050° ± 10°K — m.p. = 1745° ± 10°K

	cal °K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-2.962	-200.115	-200.115	Infinite
298.15	17.600	18.150	18.150	0.000	-201.460	-182.620	133.858
300	17.650	18.259	18.150	0.033	-201.458	-182.503	132.947
400	19.849	23.663	18.870	1.917	-201.226	-176.205	96.269
500	21.182	28.249	20.299	3.975	-200.866	-169.999	74.303
600	22.060	32.193	21.961	6.139	-200.443	-163.852	59.680
700	22.724	35.645	23.674	8.380	-199.982	-157.803	49.266
800	23.273	38.716	25.366	10.680	-199.501	-151.797	41.467
900	23.756	41.486	27.005	13.033	-198.996	-145.130	35.241
1000	24.198	44.012	28.582	15.430	-198.473	-139.986	30.592
1050	24.408	45.197	29.344	16.646	-198.207	-137.085	28.532
1050	23.678	45.587	29.344	17.056	-197.797	-137.085	28.532
1100	23.815	46.691	30.106	18.243	-197.559	-134.200	26.662
1200	24.090	48.775	31.577	20.638	-197.082	-128.438	23.391
1300	24.365	50.714	32.975	23.061	-196.603	-122.764	20.638
1400	24.640	52.530	34.308	25.511	-196.122	-117.107	18.280
1500	24.915	54.239	35.580	27.989	-195.637	-111.479	16.242
1600	25.190	55.856	36.797	30.494	-195.150	-105.883	14.462
1700	25.465	57.391	37.963	33.027	-194.659	-100.320	12.896
1745	25.589	58.058	38.473	34.176	-194.440	-97.833	12.252
1745	31.500	68.115	38.473	51.726	-176.890	-97.833	12.252
1800	31.500	69.093	39.394	53.458	-176.294	-95.344	11.576
1900	31.500	70.795	41.001	56.608	-175.232	-90.871	10.452
2000	31.500	72.411	42.532	59.758	-174.195	-86.458	9.447

in the present compilation in preference to other, older, and less accurate values.[471, 472, 478-486]

Values of ΔH_f°, ΔF_f°, and $\log_{10} K_P$ were calculated from equations (44), (251), and (252).

$$\Delta H_f^\circ = \Delta H_{f298}^\circ + (H_T^\circ - H_{298}^\circ)_{WO_{3(c)}} - (H_T^\circ - H_{298}^\circ)_{W(s)} - (3/2)(H_T^\circ - H_{298}^\circ)_{O_{2(g)}} \quad (251)$$

$$\Delta F_f^\circ = \Delta H_{f298}^\circ + (F_T^\circ - H_{298}^\circ)_{WO_{3(c)}} - (F_T^\circ - H_{298}^\circ)_{W(s)} - (3/2)(F_T^\circ - H_{298}^\circ)_{O_{2(g)}} \ . \quad (252)$$

2) Gas phase

All of the molecular constants required in the calculation of the thermodynamic functions for gaseous WO_3 have been estimated since no experimental spectroscopic data have been reported. The thermodynamic functions for gaseous WO_3 given in Table LXXIII were calculated by means of the machine program described in section III-F with the following molecular data:

Molecular configuration

Planar, symmetrical cart-wheel molecule with

$$\angle \text{O–W–O} = 120 \text{ deg}$$

$$r_o = 1.78 \text{ Å} \ .$$

Product of moments of inertia

$$I_A I_B I_C = 4024423 \times 10^{-120} g^3 cm^6 \ .$$

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[478] Huff, G., E. Squitieri, and P.E. Snyder, J. Am. Chem. Soc. 70, 3380 (1948).

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[484] Shibata, Z., Tech. Repts. Tohoku Imp. Univ. 8, 145 (1929).

[485] Gerasimov, Ya. I. and I.A. Vasil'eva, J. Chem. Phys. 56, 636 (1959).

[486] Vasil'eva, I. A., Y. Gerasimov, Ya. I. Simonov, and T. Rezukhina, Zhur. Fiz. Khim. 31, 682 (1957).

TABLE LXXIII

TUNGSTEN TRIOXIDE | IDEAL MOLECULAR GAS | O_3W

Reference State for Calculating ΔH_f°, ΔF_f°, and $\text{Log } K_p$: Solid W from 298.15° to 3650°K, Liquid W from 3650° to 5891°K, Gaseous W from 5891° to 6000°K; Gaseous O_2; Gaseous WO_3.

gfw = 231.86 | T_t = 1050° ± 10°K | m.p. = 1745° ± 10°K

	cal/°K gfw			Kcal/gfw			
T, °K	C_p°	S_T°	$-(F_T^\circ - H_{298}^\circ)/T$	$H_T^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	Infinite	-3.296	-64.089	-64.089	Infinite
298.15	14.936	68.626	68.626	0.000	-65.100	-61.309	44.939
300	14.972	68.718	68.626	0.028	-65.103	-61.286	44.645
400	16.514	73.253	69.234	1.608	-65.175	-59.990	32.776
500	17.487	77.051	70.428	3.311	-65.170	-58.703	25.658
600	18.113	80.299	71.809	5.094	-65.128	-57.401	20.907
700	18.530	83.124	73.228	6.927	-65.075	-56.131	17.524
800	18.818	85.618	74.624	8.795	-65.026	-54.843	14.982
900	19.025	87.847	75.972	10.688	-64.981	-53.591	13.013
1000	19.177	89.860	77.262	12.598	-64.945	-52.306	11.431
1100	19.292	91.693	78.492	14.522	-64.920	-51.065	10.145
1200	19.381	93.376	79.663	16.456	-64.904	-49.782	9.066
1300	19.452	94.930	80.778	18.398	-64.906	-48.549	8.161
1400	19.508	96.374	81.841	20.346	-64.927	-47.292	7.382
1500	19.554	97.721	82.855	22.299	-64.967	-46.031	6.706
1600	19.592	98.985	83.824	24.256	-65.028	-44.766	6.115
1700	19.623	100.173	84.752	26.217	-65.109	-43.500	5.592
1800	19.649	101.296	85.640	28.181	-65.211	-42.226	5.127
1900	19.672	102.359	86.492	30.147	-65.333	-40.943	4.709
2000	19.691	103.368	87.311	32.115	-65.478	-39.656	4.333
2100	19.708	104.329	88.099	34.085	-65.644	-38.359	3.992
2200	19.722	105.247	88.857	36.057	-65.832	-37.055	3.681
2300	19.735	106.124	89.589	38.029	-66.041	-35.742	3.396
2400	19.746	106.964	90.296	40.004	-66.271	-34.426	3.135
2500	19.756	107.770	90.979	41.979	-66.525	-33.093	2.893
2600	19.765	108.545	91.639	43.955	-66.800	-31.749	2.669
2700	19.772	109.291	92.279	45.932	-67.098	-30.391	2.460
2800	19.779	110.010	92.900	47.909	-67.416	-29.028	2.266
2900	19.786	110.705	93.502	49.887	-67.757	-27.652	2.084
3000	19.791	111.375	94.037	51.866	-68.119	-26.265	1.913
3100	19.797	112.024	94.655	53.846	-68.502	-24.856	1.752
3200	19.801	112.653	95.208	55.826	-68.908	-23.450	1.601
3300	19.805	113.262	95.745	57.806	-69.332	-22.014	1.458
3400	19.809	113.854	96.269	59.787	-69.780	-20.577	1.323
3500	19.813	114.428	96.780	61.768	-70.246	-19.117	1.194
3600	19.816	114.986	97.278	63.749	-70.736	-17.647	1.071
3650	19.818	115.258	97.521	64.740	-70.987	-16.907	1.012
3650	19.818	115.258	97.521	64.740	-79.382	-16.907	1.012
3700	19.819	115.529	97.764	65.731	-79.626	-16.058	0.948
3800	19.822	116.058	98.239	67.713	-80.121	-14.334	0.824
3900	19.824	116.573	98.702	69.695	-80.623	-12.589	0.705
4000	19.827	117.075	99.155	71.678	-81.128	-10.836	0.592
4100	19.829	117.564	99.598	73.661	-81.639	-9.077	0.484
4200	19.831	118.042	100.032	75.644	-82.156	-7.300	0.380
4300	19.833	118.509	100.456	77.627	-82.677	-5.504	0.280
4400	19.835	118.965	100.871	79.610	-83.207	-3.696	0.184
4500	19.836	119.410	101.279	81.594	-83.739	-1.899	0.092
4600	19.838	119.846	101.677	83.578	-84.279	-0.060	0.003
4700	19.839	120.273	102.069	85.561	-84.828	1.772	-0.082
4800	19.841	120.691	102.452	87.545	-85.384	3.634	-0.165
4900	19.842	121.100	102.829	89.530	-85.949	5.483	-0.245
5000	19.843	121.501	103.198	91.514	-86.526	7.365	-0.322
5100	19.844	121.894	103.561	93.498	-87.117	9.241	-0.396
5200	19.845	122.279	103.917	95.483	-87.722	11.149	-0.469
5300	19.846	122.657	104.267	97.467	-88.348	13.054	-0.538
5400	19.847	123.028	104.611	99.452	-88.995	14.980	-0.606
5500	19.848	123.392	104.949	101.437	-89.667	16.918	-0.672
5600	19.849	123.750	105.282	103.422	-90.373	18.855	-0.736
5700	19.850	124.101	105.609	105.407	-91.116	20.822	-0.798
5800	19.851	124.447	105.931	107.392	-91.907	22.800	-0.859
5891	19.852	124.755	106.219	109.198	-92.677	24.613	-0.913
5891	19.852	124.755	106.219	109.198	-284.942	24.613	-0.913
5900	19.852	124.786	106.247	109.377	-285.015	25.087	-0.929
6000	19.852	125.120	106.559	111.362	-285.900	30.360	-1.106

Symmetry number

$\theta = 6$.

Fundamental frequencies

$\omega_1 = 780\ cm^{-1}$

$\omega_2 = 298\ cm^{-1}$

$\omega_3 = 791\ cm^{-1}$ (2)

$\omega_4 = 314\ cm^{-1}$ (2)

Ground electronic state

$^1\Sigma$

The above molecular constants were estimated by the procedures employed in the case of the corresponding CrO_3 molecule (see section IV-B3b). The W-O bond distance was assumed to be the same as the estimated distance for the corresponding bond in WO;[401] i.e., 1.78Å. The estimated fundamental frequencies above are somewhat lower than those of DeMaria and co-workers[410] and of Ackermann and Thorn.[487]

The standard enthalpy of formation, ΔH°_{f298}, of gaseous WO_3 had not been directly determined, and was therefore determined by the indirect method employed in the case of MoO_3 (see section IV-B5c) based on the mass spectrographic study of Al_2O_3 in tungsten containers by DeMaria and co-workers.[410] The value of the heat of formation so obtained was -65,100 $\pm$ 5000 cal/gfw. $H^\circ_{298}-H^\circ_0$ for gaseous WO_3 was found to be 3296 cal/gfw.

Values of ΔH°_f, ΔF°_f, and $\log_{10} K_p$ were calculated in an analogous fashion to that described in section IV-B5c for the corresponding MoO_3 molecule.

[487] Ackermann, R.J. and R.J. Thorn, U.S. AEC Rept. ANL-5824 (January 1958).

V. EXPERIMENTAL STUDIES

A. PREPARATION AND ANALYSIS OF COMPOUNDS AND SPECIMENS

1. The three following methods were used to obtain specimens for heat capacity measurements:

a. Solid pieces of various refractory compounds were obtained from commerical sources and machined to specifications by the use of diamond tools and electric discharge (Elox) techniques. Materials obtained in this way were titanium diboride, zirconium diboride, tungsten boride, molybdenum boride, molybdenum carbide, titanium carbide, and zirconium carbide (all obtainedfrom Carborundum Co.) and titanium metal (obtained from Foote Mineral Co.). X-ray diffraction analysis showed that the molybdenum boride and carbide specimens were multiphase systems, and further analyses were, therefore, discontinued. In the case of all the other specimens however, complete X-ray and chemical analyses were performed. The results are given with the heat capacity data for the respective specimens in section V-B, 4 below.

b. Materials were also obtained in the form of powders from commercial sources and fabricated into solid bodies which were subsequently machined to specifications. In most cases, the fabrication was accomplished by hot pressing the powders in graphite dies at temperatures above 1300°C and at pressures of from 2000 to 2500 psi. The details of the fabrication of each specimen are given in Table LXXIV.

Attempts to prepare elemental boron specimens by hot pressing in graphite dies with and without boron nitride liners and punches were unsuccessful. However, sound bodies were prepared by a cold-pressing and sintering technique. Boron powder was mixed with a small amount of stearic acid and compacted by cold pressing at 20,000 psi. The stearic acid was eliminated by heating at 400°F, and the boron body was then sintered at 1300°C for 2 hours in an argon atmosphere. Rods, 0.5 inch in diameter and 1-1/2 inches in length with a density between 1.30 and 1.38 g/cc, were fabricated by this method. β-rhombohedral boron was the only phase detected in these specimens, but there was an increase of 0.8 percent in carbon content over that detected in the original boron powder. This increase was probably due to incomplete elimination of the stearic acid binder.

c. Work was also started on the laboratory preparation of compounds. Silicon hexaboride, tantalum boride, and tantalum nitride were prepared in small quantities from the elements.

2. Chemical Analysis

a. Oxygen Determination

The need for a rapid, accurate, and reliable method for the determination of oxygen in refractory compounds motivated the development and adaption of the inert-gas fusion method to this problem. Vacuum fusion and vacuum extraction have both been used in the past, but they did not lend themselves to rapid determinations. Often, in the past, the oxygen content was not determined but estimated as the difference between the major-constituents analysis and 100 percent.

Figure 5 is a schematic diagram of the apparatus fabricated for the inert-gas fusion method of determining oxygen in refractory materials. Argon was passed through a purifying train (containing "Ascarite", concentrated sulfuric acid, and heated titanium metal chips) and then, to a flow-regulating valve and meter. A pressure-relief valve was used to maintain a constant pressure throughout the system. The argon flowed to the main furnace chamber which contained a high-purity (spectrographically pure) graphite crucible packed in powdered graphite. The crucible contained a platinum bath and was maintained at 2100°C by means of induction heating. After outgassing of the system by heating until the blank run gave constant results, the platium bath was allowed to become saturated with carbon from the graphite crucible before the specimen was introduced.

A sample of 10 to 60 milligrams of finely ground refractory compound was weighed in a small, high-purity tin capsule which served as a vehicle. The sample was inserted in the furnace by means of a loading valve. The oxygen in the sample reacted with the carbon in the platinum bath to form carbon monoxide which was entrained by the flow of argon. The gases then passed through a tube containing copper oxide maintained at 750°C. The carbon monoxide was thus converted to carbon dioxide which was then carried to the conductimetric carbon determinator where the CO_2 was absorbed and measured.

The conductometric carbon determinator functioned on the principle of a Wheatstone bridge, measuring the conductivity of a barium hydroxide solution. The argon gas carrying the carbon dioxide was dispersed through the solution where the CO_2 and $Ba(OH)_2$ reacted to form barium carbonate, thus changing the conductivity of the solution by an amount which was a measure of the CO_2 absorbed.

Oxygen analyses were performed on five samples of unalloyed titanium, which were received from the Watertown Arsenal, to check the validity of the inert-gas fusion method of oxygen determination. These samples were previously analyzed for oxygen by a task force of 15 different laboratories. The results confirm the validity of the inert-gas fusion method used at Avco RAD.

TABLE LXXIV

CONDITIONS OF REFRACTORY POWDER HOT PRESSING

Material	Source	Lot No.	Temperature °C	Pressure psi	Time hours	Density of Piece g/cc	Theoretical Density g/cc
TaC	Starck	TAP-991 TaC	1350	2000	1	13.2	14.5
TaC	Starck	Grade I	1500	2500	3	13.39	14.5
NbC	Starck	931/c/3	1500	2500	2-1/2	6.96	7.8
NbC	Starck	134/B	1300	2500	1	7 08	7.8
CrB_2	Starck	ax-3159	1600	2500	1	---	5.6
W_2B_5	Starck	TAP-151/B	1600	2500	2	8.14	10.77
MoB	Starck	151/D	1600	2500	2	7.05	8.8
HfC	Wah Chang	R. D. 10603K	1800	2500	1	8.45	12.7
MoC	A. D. MacKay	MoC -100	1600	2500	2	7.3	8.4

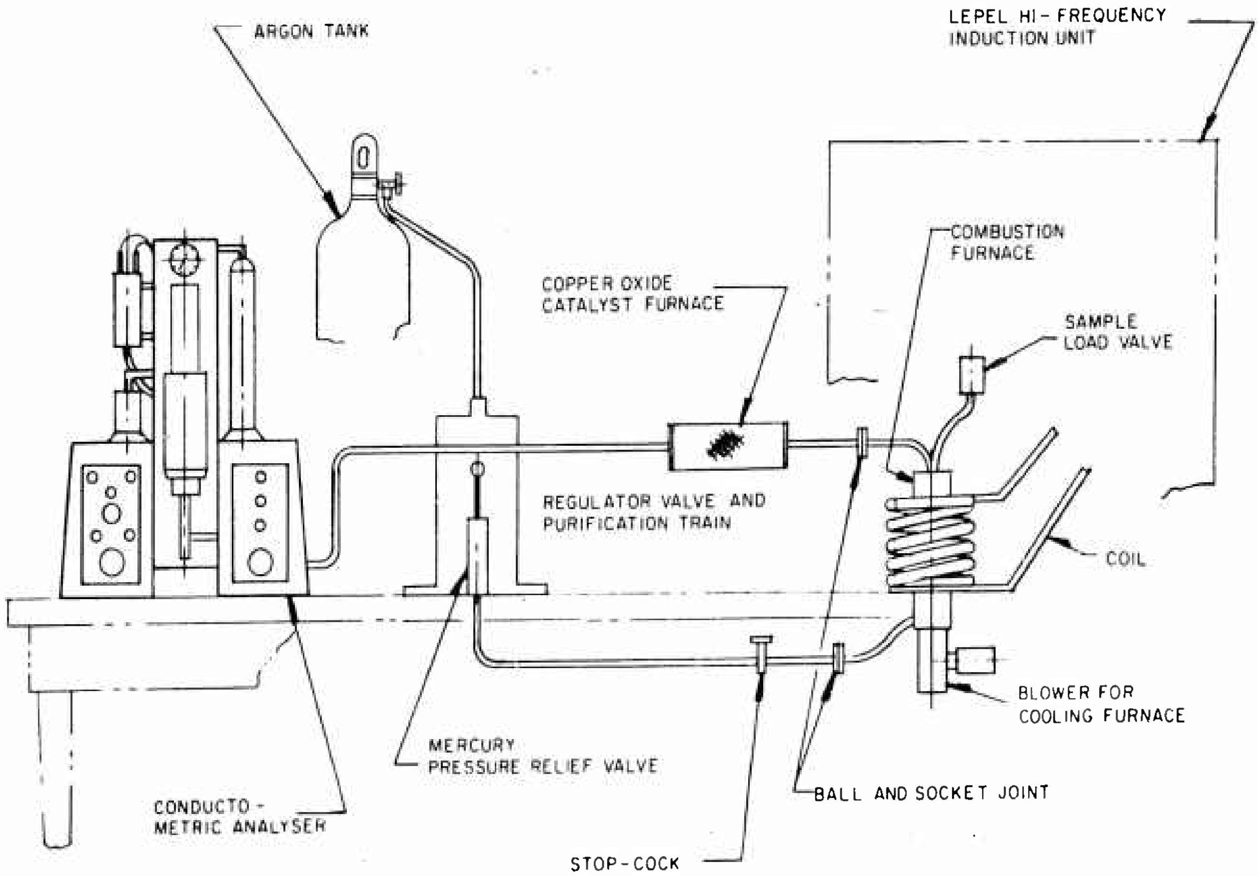


Figure 5 SCHEMATIC OF INERT-GAS FUSION APPARATUS

b. After dissolution by one of the usual methods as required (i.e., acid, fusion and leaching, etc.), metal determinations were made as follows:

1) Titanium with Jones Reductor (zinc amalgam) and titration with potassium dichromate

A solution of the titanium (Ti^{+++}) was passed through a standard Jones reductor where the titanium was reduced to Ti^{++}. The resulting solution, containing the reduced titanium, was then titrated with an oxidizing agent (potassium dichromate). The titanium content was calculated from the standard value of titanium for the volume of the dichromate solution used.

2) Chromium by oxidation with perchloric acid and titration of the resulting dichromate

The chromium solution was oxidized to a dichromate solution by heating to fumes in perchloric acid. The oxidized solution was then cooled and titrated with a reducing solution (ferrous ammonium sulphate) for which a standard chromium value had been previously established.

3) Molybdenum by precipitation with alphabenzoinoxime

The sample containg molybdenum was dissolved and alphabenzoinoxime solution was added. The molybdenum was thus precipitated as the organic complex. The precipitate was then filtered and dried to constant weight. The molybdenum content was then computed from the weight of the precipitate in the usual way.

4) Tungsten by precipitation with cinchonine

The tungsten compound was dissolved by means of an alkali fusion. A solution of cinchonine was then added to the tungsten solution and the mixture heated gently to precipitate the tungsten complex. This precipitate was then filtered and dried to constant weight. The amount of tungsten was then computed in the usual way from the weight of the precipitate.

5) Niobium, tantalum, and hafnium by separation from other metals by ion exchange and gravimetric determination as the oxide

Niobium, tantalum and hafnium compounds were put into an acid solution, and passed through a resin column where the metals were absorbed. By means of varying acid strengths, the metals were selectively eluded from the resin. The individual solutions were brought to dryness, and the metals were converted to oxides by standard ashing techniques. The weight of the metal oxide was then computed and converted to the weight of the metal.

c. Nonmetal determinations were made as follows:

1) Boron by conversion to acid with mannitol and titration

The boron compound was converted to soluble boric acid by means of alkali fusion. Mannitol or glycerine was added to the boric acid solution to form a readily titratable solution with sodium hydroxide. The boron content was computed from the amount and the standard value of the sodium hydroxide solution required for neutralization.

2) Nitrogen by Kjeldahl digestion and titration

The nitrogen compound was dissolved by means of acid digestion in a Kjeldahl flask. The flask was then transfered to a Kjeldahl distillation apparatus where the nitrogen-containing solution was made ammoniacal by addition of caustic solution. The ammonia thus formed was distilled and trapped in distilled water. The resultant solution was then titrated with a standard hydrochloric acid solution.

3) Carbon by combustion and volumetric measurement of liberated CO_2 with a Leco apparatus

The total carbon was determined volumetrically by means of a Leco combustion furnace and a Leco volumetric carbon determinator.

The free carbon was determined by means of combustion in air at a temperature below the decomposition temperature of the carbide. Thus, the loss in weight was a direct measure of the free carbon content. The combined-carbon content was obtained by difference from these two results.

d. Trace-Impurity Determinations

Spectrographic analytical curves for known concentrations of trace impurities in refractory compounds had been established, and it was possible to determine quantitatively the concentrations of the trace impurities.

3. X-Ray Diffraction Analysis

Diffraction diagrams of the specimens were obtained with a 114.59 mm Debye-Scherrer camera with Ni-filtered Cu radiation. Lattice constants calculated from reflections above θ = 50 degrees were plotted against $\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}$, and the best straight-line fit (visual) was extrapolated to θ = 90 degrees for the lattice constant. The precision of the measurements was (± 0.0005Å). The results for the individual heat capacity measurement specimens are given with the heat capacity data in section V-B below.

Reaction between the specimens and the carbon vapor in the high-temperature heat capacity furnace was first noticed in the case of TiN. The outer surface of the specimen turned blue, and the lattice constant of this blue material was found to be larger than that of the starting TiN. Drillings were then taken (perpendicular to the rod axis) to a depth of approximately 1.60 mm and the X-ray measurement repeated to reveal the depth of carbon penetration. Results are summarized in Table LXXV.

TABLE LXXV

VARIATION OF LATTICE CONSTANT VERSUS DEPTH IN TiN SPECIMENS AFTER HIGH-TEMPERATURE HEAT CAPACITY DETERMINATION

Lattice Constant (Å)	Approximate Composition	Depth (mm)
4.28	$TiN_{0.5}C_{0.5}$	0.40
4.27	$TiN_{0.65}C_{0.35}$	0.80
4.24	TiN	1.20
4.24	TiN	1.60

Carbon concentrations were calculated on the basis of the following assumptions. (a) all the nonmetal sites were filled, and (b) the TiN - TiC solid solutions obey Vegard's straight-line relationship. Subsequent analyses on other specimens revealed carbide layers of 0.4 mm (TiC) in the case of TiB_2, and 0.3 mm (WC) in the case of WB. The presence of ZrC was also found on the surface of the ZrB_2 specimen.

The presence of tungsten carbides at the contact areas of the TaC and NbC specimens with the tungsten electrodes and the absence of them in the TiN case indicated the possibility of some reaction between the tungsten and carbide specimens only.

The TiC, TaC, and NbC specimens were found in post-test analyses to be one-phase systems of the same lattice constants as the starting materials (except for a slight lattice-constant increase on the surface, probably due to increased carbonization). The ZrC specimen exhibited weak reflections of ZrO_2 similar to those of the starting material.

Since the first NbC specimen showed unusual behavior in the specific heat measurements, a second specimen (931C) was prepared and characterized. The lattice constant of the first NbC specimen was 4.4673Å. This corresponded to a C/Nb ratio of 0.93 according to the data of Kempter and Storms.[488] Since chemical analyses had also been made, it was possible to check the X-ray result. The analytical data on NbC are summarized in Table LXXVI. The C/Nb ratios obtained by chemical analysis were calculated directly from the total niobium (or niobium plus tantalum where tantalum is not reported). In most cases, the diffraction pattern indicated extremely weak additional reflections in the front-reflection region that could be indexed (although with some ambiguity because of their weak diffuse intensity) as Nb_2O_5. It was, therefore, assumed that the majority of the oxygen reported by chemical analysis was not in solution with the NbC although the nitrogen and tantalum were, since there was no indication of NbN or Ta in the X-ray diagrams. The lattice constants reported are not corrected for the decrease due to tantalum in solution (approximately 0.0003Å per percent Ta) or the increase due to nitrogen in solution (approximately equal to a corresponding amount of carbon, assuming the carbon radius to be 0.76Å and the nitrogen radius to be 0.71Å).[448]

[488] Kempter, C. and E. K. Storms, J. Chem. Phys. 33, 1873 (1960).

TABLE LXXVI

NbC LATTICE CONSTANT AND CHEMICAL ANALYSIS SUMMARY

Specimen Code	Lattice Constant	C/Nb From Kempter and Storms' [488] Data	C/Nb by Chem. Anal.		Ta Content by Chem. Anal.		Avco Analysis of Other Impurities	
			Avco	Shieldalloy	Avco	Shieldalloy	Oxygen	Nitrogen
	Å				Percent	Percent	Percent	Percent
946A	4.468_7	0.95	0.96	0.96	2.12	1.80	0.12	0.29
952C	4.467_0	0.92	0.88	0.93	---	2.0	---	---
C-2453	4.468_8	0.95	0.94	---	---	---	---	---
946B	4.468_5	0.95	0.97	0.97	2.32	1.82	0.26	0.29
931C	4.468_4	0.945	0.96	0.96	1.84	1.95	0.21	0.43
134B	4.467_5	0.93	0.94	0.96	0.16	0.14	0.25	< 0.01

B. SPECIFIC HEAT DETERMINATIONS

1. Introduction

Two experimental techniques were adopted for specific heat determinations. The two were used because of the broad temperature coverage required and the inherent limitations of each system.

The Bunsen type of ice calorimeter[489] shown in figure 6 was chosen for "low" temperature determinations (room temperature to 1900°C). The maximum temperature of operation for this apparatus is determined by the radiant heat transfer from the associated furnace to the calorimeter and by other losses that occur with the transfer of the sample from the furnace to the calorimeter. The photograph in figure 7 shows a cutaway view of internal details of the calorimeter chamber.

A modified pulse technique was adopted for the high-temperature determinations of specific heat. The technique used is similar to that of Rasor and McClelland.[27] The practical limits of temperature coverage of this "high" temperature apparatus shown in figure 8 are approximately 1800° to 3900°K.

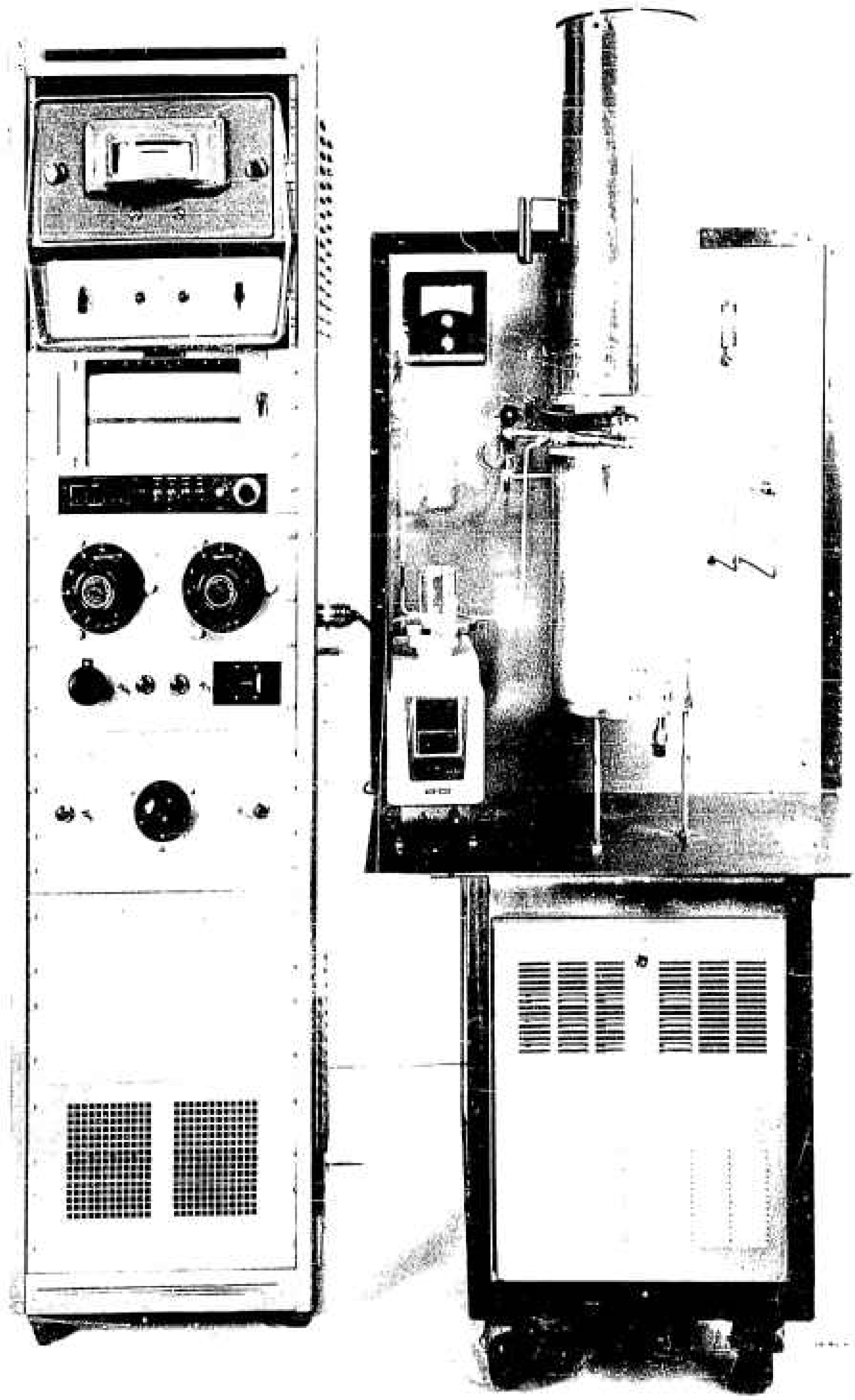
Considerable care was exercised to ensure the accuracy of temperature measurements throughout the specific heat measurements. Secondary calibration standards were continuously maintained in the laboratory, and frequent calibration checks were made of the instruments. The calibration standards used were a gold melting-point apparatus, NBS-certified tungsten strip lamps, NBS-certified freezing point metals, an NBS-certified platinum-resistance thermometer, and platinum - platinum 10 percent rhodium thermocouples with the associated NBS-certified Müller bridge and Werner potentiometer.

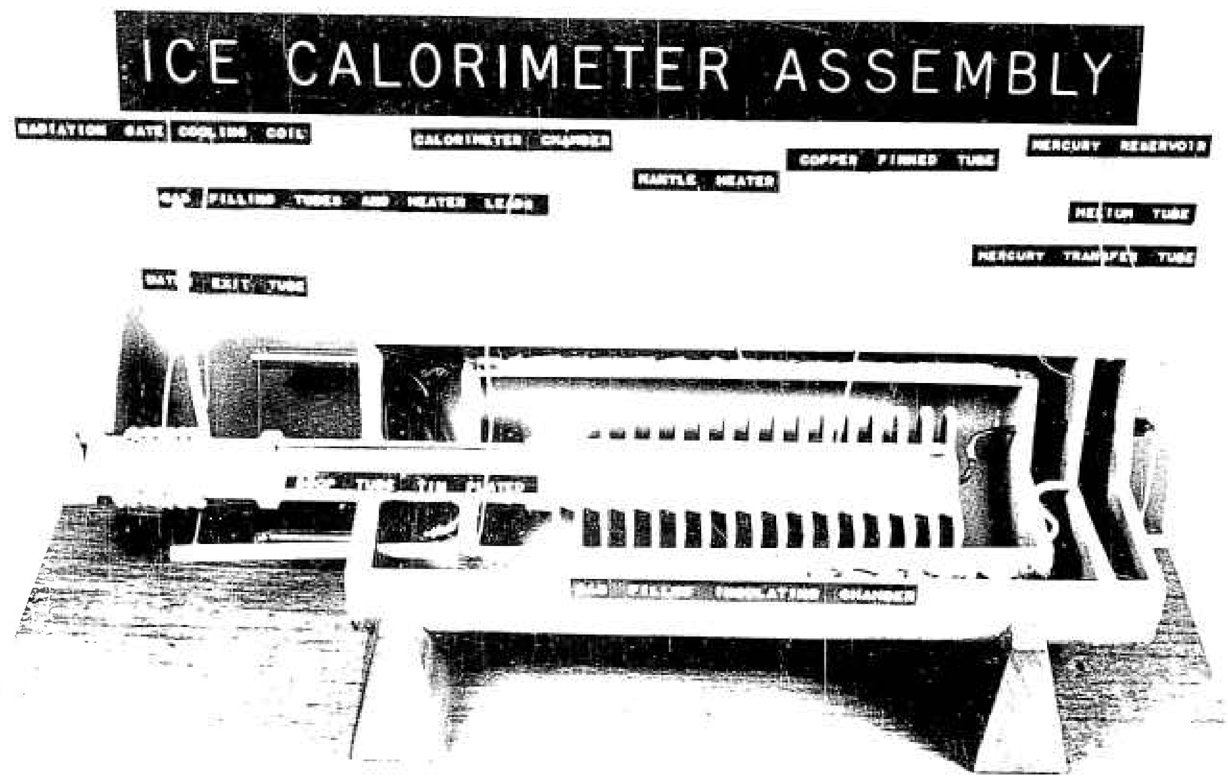
An extended range, DK-2, ratio-recording spectrophotometer was used to determine the transmissivity characteristics of any associated glass or quartz windows used during the experimental determinations.

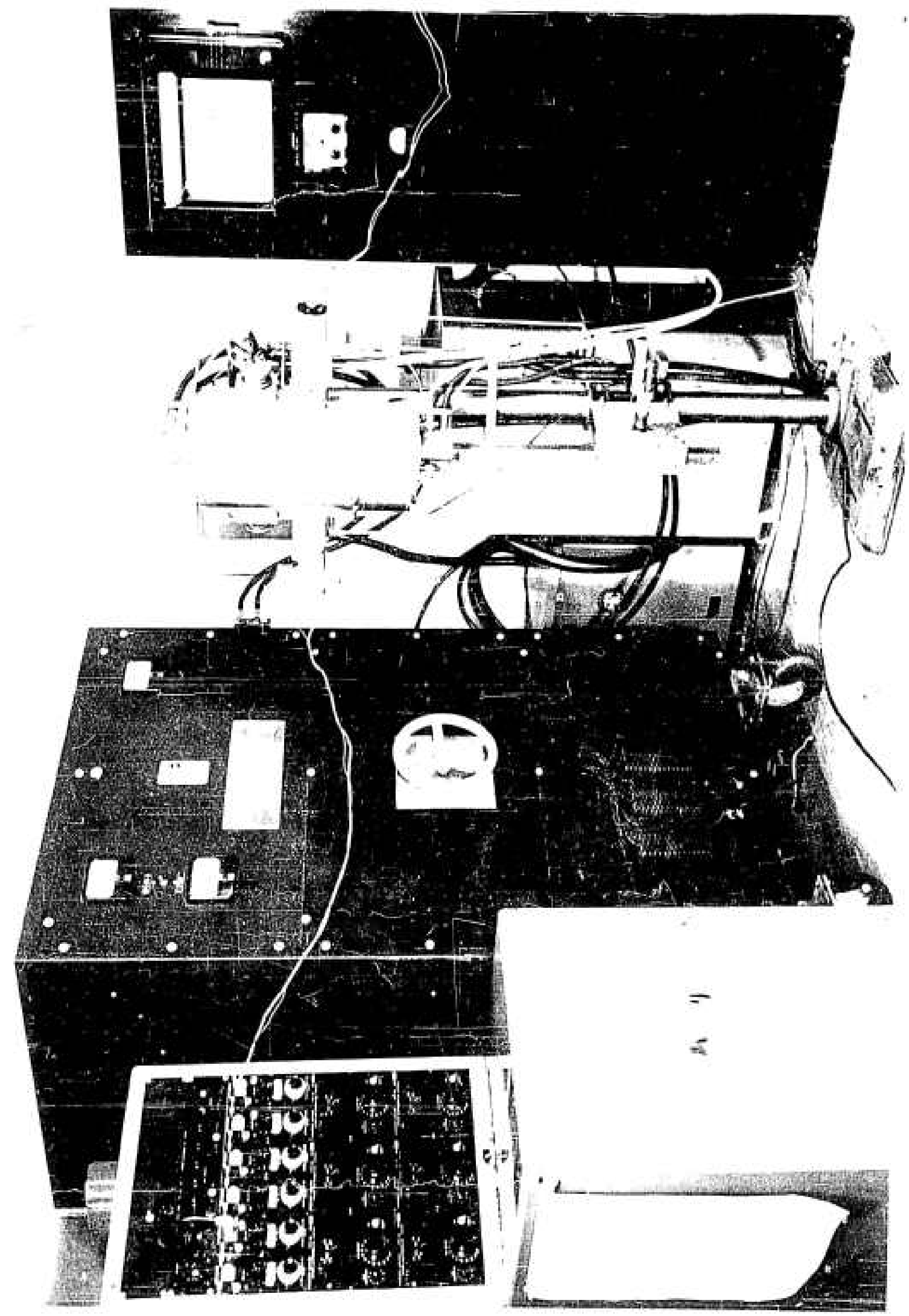
2. The Bunsen Ice Calorimeter

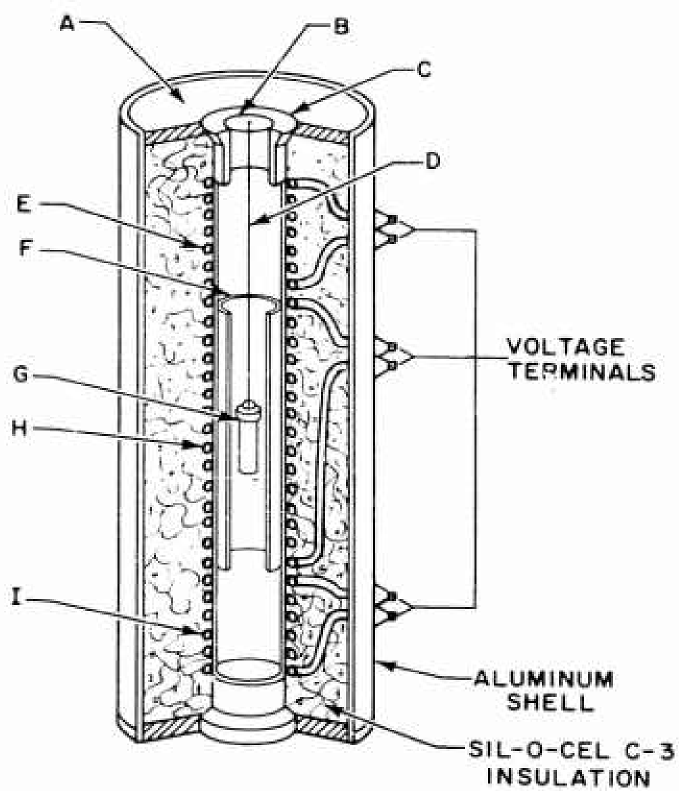
The Bunsen ice calorimeter is extensively used to make specific heat determinations in a number of laboratories. A few innovations were introduced into the one used for this work. The designs of the furnace and calorimeter components are shown schematically in figures 9 and 10.

[489] Deem, H. W. and C. F. Lucks, An Improved All Metal Bunsen Type Ice Calorimeter, ISA Conference Paper, PPT-4-58-1 (September 1958).




ICE CALORIMETER ASSEMBLY
RADIATION GATE
COOLING COIL
CALORIMETER CHAMBER
MANTLE HEATER
COPPER FINNED TUBE
MERCURY RESERVOIR
GAS FILLING TUBES AND HEATER LEADS
MERCURY TRANSFER TUBE
EXIT TUBE





A-END PLATE (LAVA)
B-RELEASE WASHER (SS304)
C-ALIGNMENT HUB (AL_2O_3)
D-SUSPENSION WIRE (KANTHAL "A")
E-RESISTANCE WINDING-END (KANTHAL "A")
F-STABILIZING BLOCK-(INCONEL) WITH SIX THERMOCOUPLES
G-SAMPLE HOLDER (SS-304) WITH CENTRAL THERMOCOUPLE
H-RESISTANCE WINDING-CENTER (KANTHAL "A")
I-RESISTANCE WINDING-END (KANTHAL "A")

Figure 9 ICE CALORIMETER FURNACE

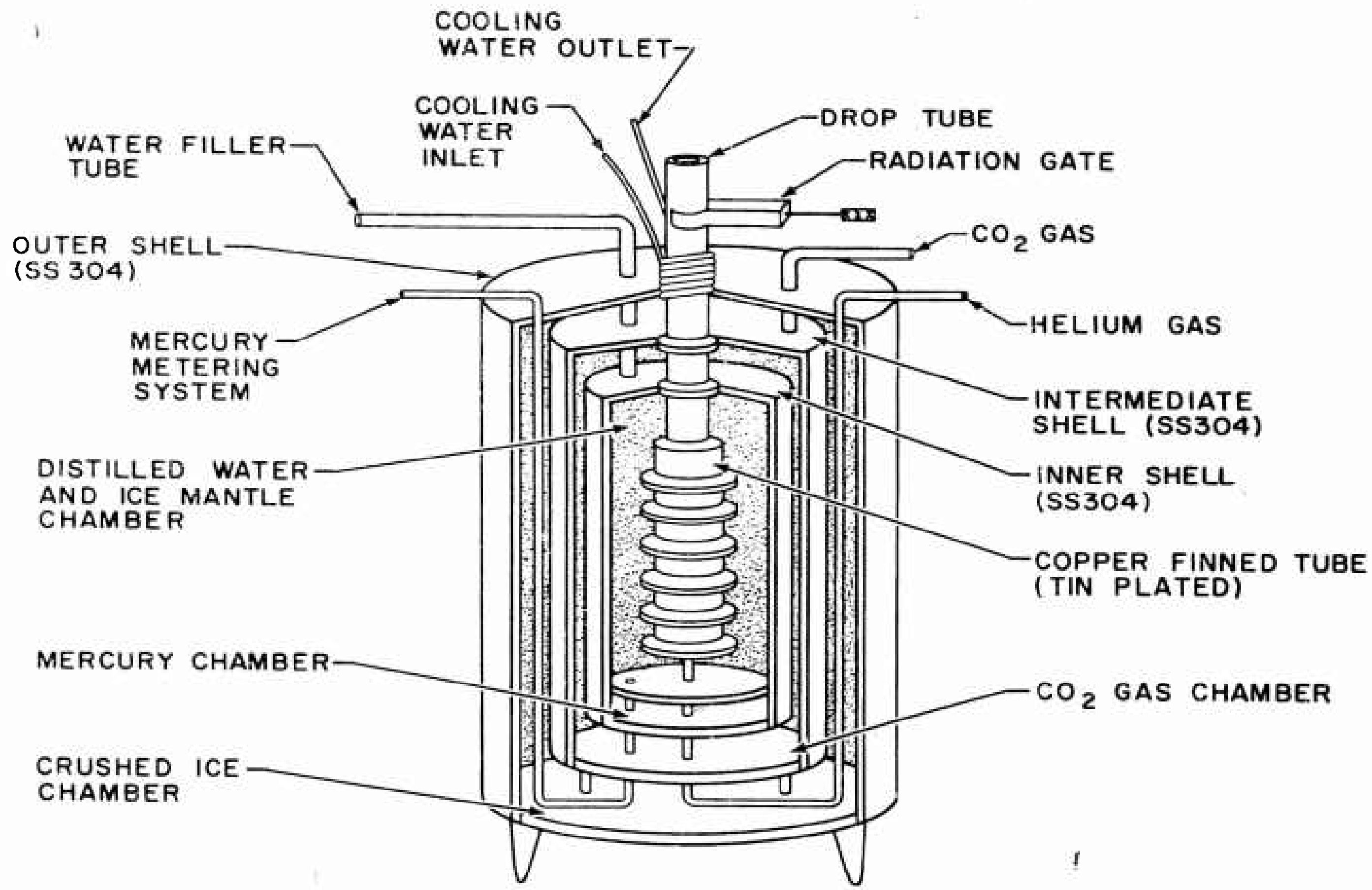


Figure 10 BUNSEN ICE CALORIMETER

The furnace was multiply wound with separate controls associated with each winding. The end windings allowed for the usual end losses and permitted a long hot zone in the vicinity of specimen heating.

A stabilizing slug, (F) in figure 9, was also used along the central furnace area to improve the temperature gradient characteristics. There were seven thermocouples of the platinum - platinum 10 percent rhodium variety located in the vicinity of the furnace center to provide continuous monitoring of the sample area temperature. The distribution of thermocouples consisted of two at the furnace center, located in opposite positions at 0 and 180 degrees; two located 2 inches above the center at 90 and 270 degrees; two located 2 inches below the center at 45 and 225 degrees;and one which traversed the center of the furnace and was inserted in a hole in the sample container (G).

The sample, placed in the sample container in a helium atmosphere, was held in position by a suspension wire (D) and the release washer (B). The release washer was held by an electromagnetic coil until the drop temperature was reached and stabilized.

Considerable care had to be used in the construction of the calorimeter drop tube because of the tendency for failures to occur at joints between dissimilar metals. The finned tube assembly had to be made from a solid copper rod to eliminate the need for welded joints at the bottom plug. A graded weld was found to be necessary to attach the copper, finned tube to the stainless steel at the top of the drop tube.

Located at the top of the drop tube was a silvered radiation gate which was opened prior to, and closed immediately following, a drop to prevent radiant heat transfer. A cooling coil was also incorporated with the drop tube to reduce the heat conduction from the furnace to the calorimeter.

In operation, the inner container to which the drop tube is welded was filled with gas-free water through the water-filler tube. After filling of the entire inner chamber with water, mercury was admitted through the mercury-metering system until it filled the mercury chamber and rose approximately three-fourths of an inch in the water chamber. The latter operation displaced water which flowed out through the water-filler tube. The water-filler tube was then sealed off by means of a suitable valve. The system then expelled mercury when ice was formed from cooling of the water in the inner container.

At first, ice mantles were formed on the finned tube by lowering a container of dry ice into the drop tube and oscillating it over the tube length until a sufficient thickness of ice was formed. Later, it was found to be more convenient to form the mantle by injecting into the lower drop tube area a flow of air which had been pre-cooled by passing through a copper coil immersed in liquid air. This reduced the time required for mantle formation from two days to approximately two hours.

The amount of mercury displaced during melting (or additional freezing) of the previously formed ice mantle after a sample drop gave a measure of the enthalpy change.

CO_2 gas in the intermediate container shown in figure 10 reduced heat leakage to the inner container because of the gas' low thermal conductivity. The entire inner calorimeter assembly was kept at a temperature of approximately 273°K during operation by crushed ice between the outer and intermediate shells. The mercury-metering tube and the helium gas tube were passed through the crushed-ice bath to pre-cool the fluids. The helium gas was passed up the drop tube since its presence assisted in the heat transfer from the sample container to the copper finned tube. A negligible amount of heat was carried away by the helium.

A number of checkout tests were run on the Bunsen ice calorimeter apparatus. One important test was conducted on the heat-leak rate and its effect on the life of the ice mantle. Heat-leak values, as evaluated from short time observations, are plotted in figure 11. The average value of the heat-leak rate from the short-time observations (taken as representative for normal operating conditions) was determined to be 2.06 cal/hr or 18.84 grams of mercury per day using a calibration factor of 62.560 cal/g.

From the results in figure 12, it appears that a heat-leak value of 5.77 cal/hr or 52.8 grams of mercury per day is applicable in the case of long-term tests (not normally used). The higher leak rate for the long-term tests was ascribed to the depletion of ice during over-night interruptions of the experiments.

The lower value was chosen as the characteristic heat-leak rate under actual test conditions where ice depletion will not occur. The latter value is sufficiently low to indicate a negligible effect upon specific heat measurements in the apparatus regardless of furnace alignment or temperature. The further precaution was taken of adopting the standard procedure of moving the furnace away from the drop tube after a sample drop (corresponding to the case of no furnace alignment in figure 11). Further tests planned for the future included some at higher furnace temperatures.

Another test revealed that the average temperature reading of the six thermocouples in the sample region of the furnace could not be used as the drop temperature. It was therefore decided to incorporate a permanent thermocouple in such a way as to read the temperature in a small well in the capsule for this measurement.

A brief study was made of the properties of the drop-capsule material. The results are summarized in Table LXXVII.

The calorimeter was calibrated with synthetic sapphire as a standard which had been established by the measurements of Ginnings and Furukawa.[28] As a result of 12 determinations at approximately 450°K, the calibration factor was found to be 62.560 ± 0.675 cal/g of mercury or 261.707 ± 2.824 international joules/g of mercury. The factor is lower by 3.20 percent than

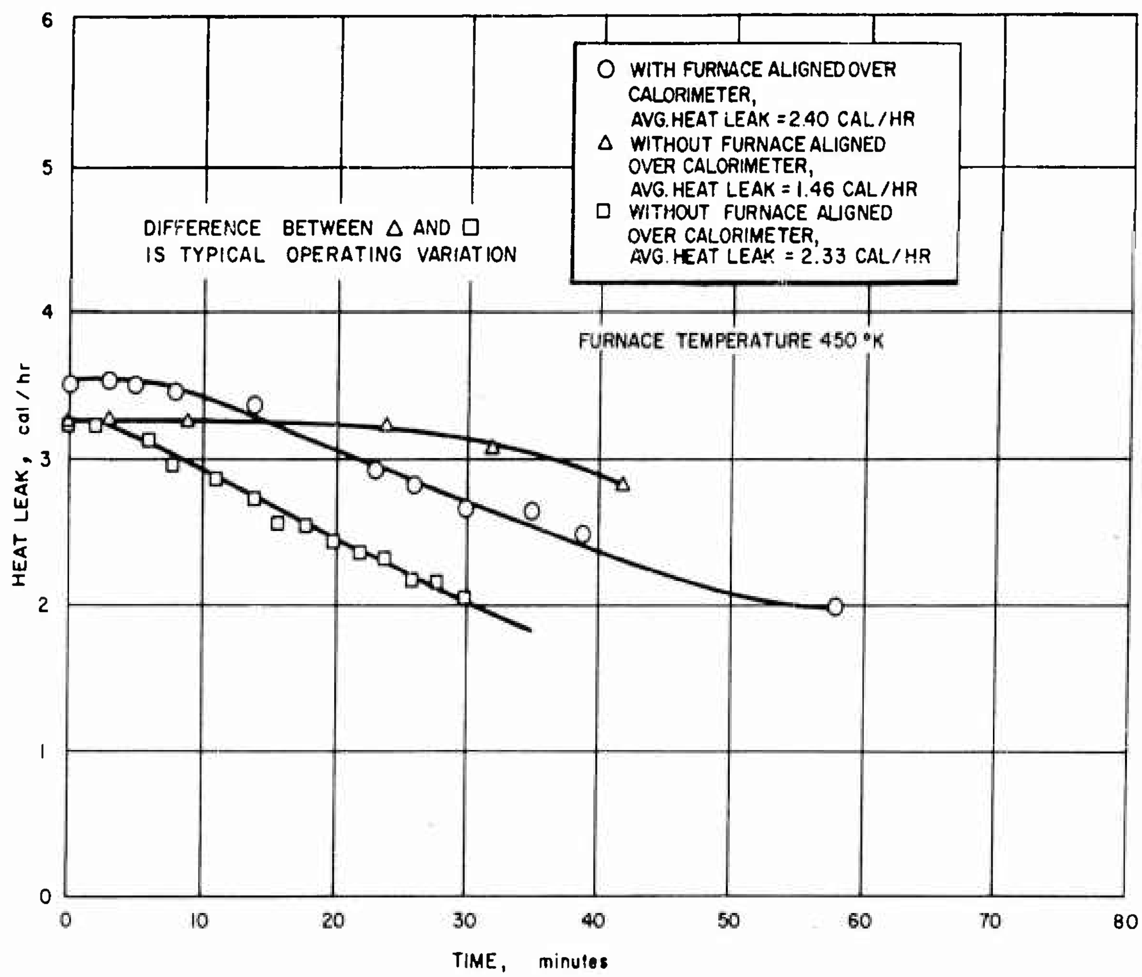


Figure 11 HEAT-LEAK CHARACTERISTICS OF AVCO BUNSEN ICE CALORIMETER

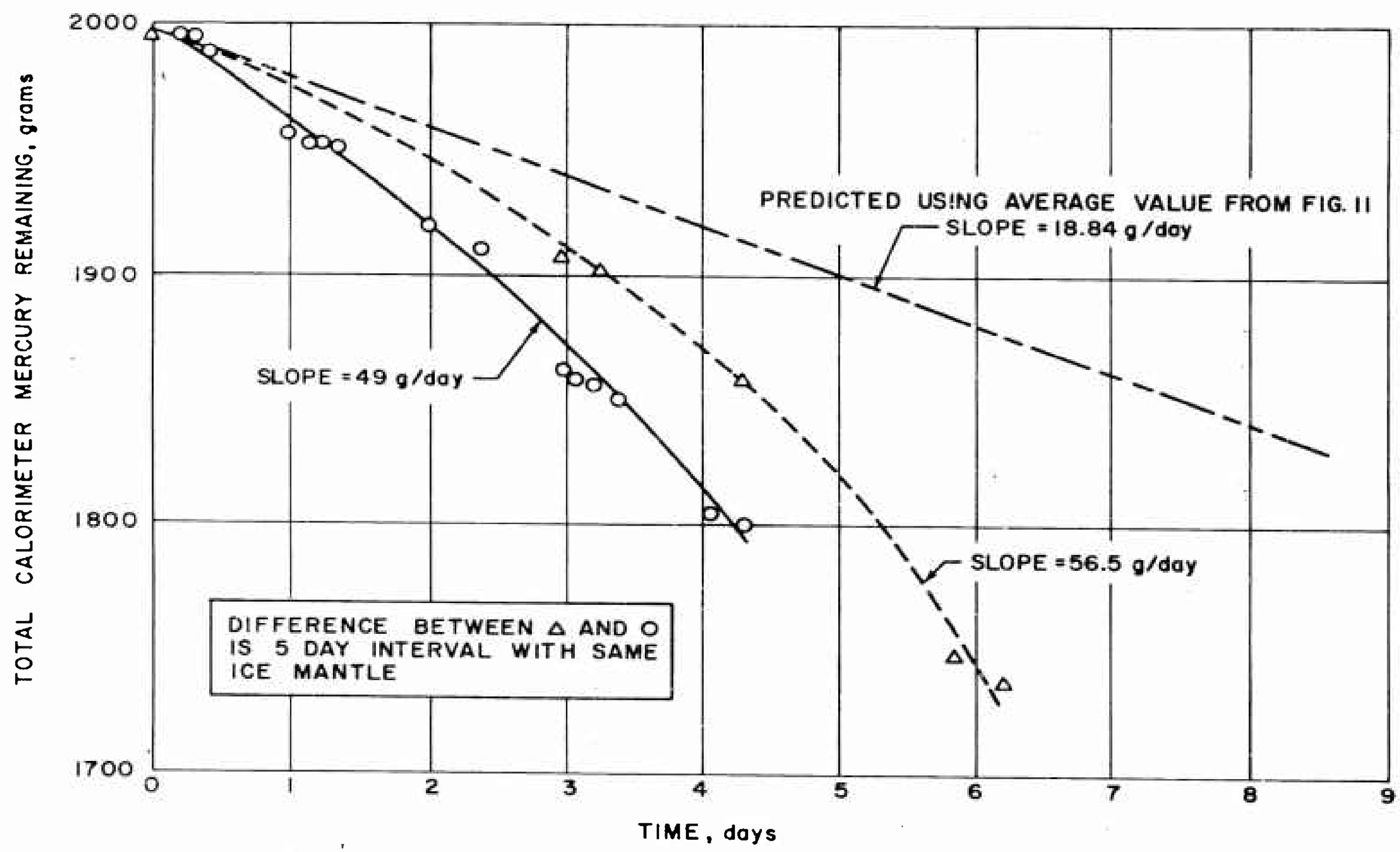


Figure 12 BUNSEN ICE CALORIMETER ICE MANTLE LIFE AS INFLUENCED BY HEAT LEAK AT NORMAL AMBIENT TEMPERATURE OF 294° K

TABLE LXXVII

SPECIFIC HEAT OF BUNSEN ICE CALORIMETER SAMPLE CAPSULE*

OVER A LIMITED TEMPERATURE RANGE

Temperature °K	Change in Enthalpy** cal/g	Specific Heat cal/°K g
325	4.843	0.094
324	5.160	0.101
403	14.213	0.109
400	14.676	0.116
399	13.570	0.108
398	13.124	0.105
396	14.656	0.119
405	14.276	0.108
401	13.326	0.104
Average values		
324.5	5.001	0.097
400.3	13.977	0.110

*Capsule was of type 304 stainless steel with a 0.030-inch thick aluminum sealing washer. Capsule weight was 19.764 grams included herein.

**Using a calibration factor of 62.560 cal/g of displaced mercury.

the value of Ginnings and Corrucini[30] of 270.37 $\pm$ 0.06 international joules/g of mercury. Electrical calibration will be used to determine whether this uncertainty is inherent in the use of synthetic sapphire as a calibration standard.

3. High-Temperature Pulse Method of Specific Heat Determination

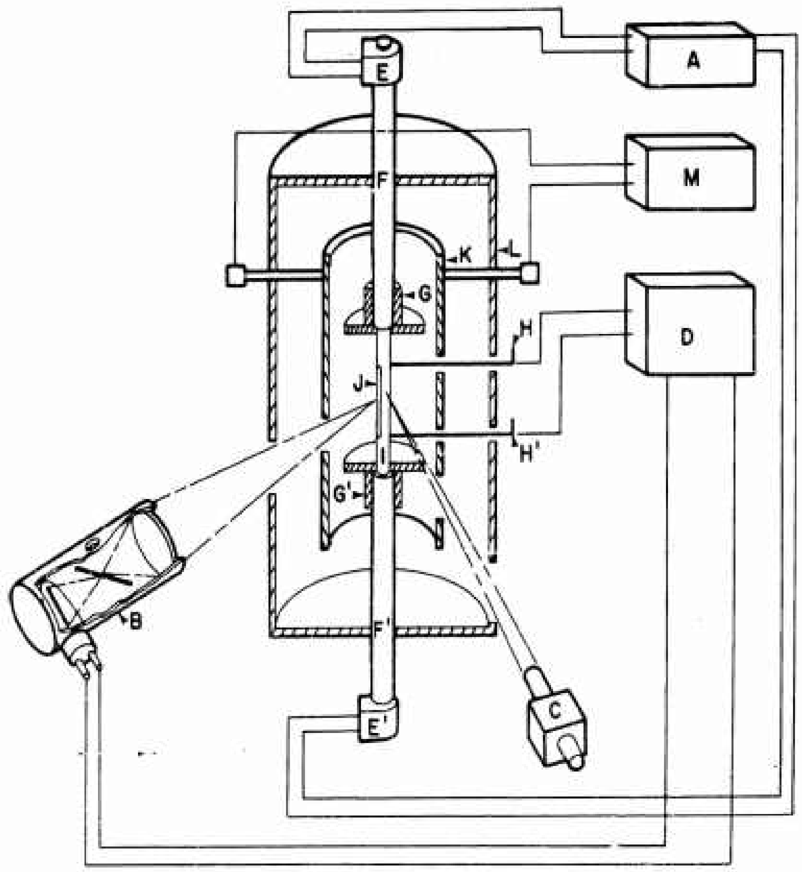
The pulse-method apparatus used for high-temperature specific heat measurements is illustrated schematically in figure 13. This apparatus was used at temperatures above 1900°K because radiative and convective losses make it very difficult to use the drop method at such high temperatures.

The furnace used in the pulse-method apparatus was of the graphite-resistance type with a flowing helium atmosphere. The original working chamber, 4 inches in diameter by 8 inches in length, was capable of operation at temperatures up to 3000°K when used as designed. As adapted for specific heat determinations however, the maximum operating temperature was found to be 2600°K.

Since the inside of the furnace chamber is essentially a blackbody enclosure, emissivity corrections were not needed for optical pyrometer temperature determinations on enclosed samples.

The operating procedure was first to heat the sample with the furnace heater (K) to the desired temperature. Power for the heaters was supplied by a 20 kilowatt a-c source (M), capable of raising the furnace temperature to nearly 2500°K in a period of about 30 minutes. After sufficient time for the ambient temperature to stabilize, a high current from the d-c power supply (A) was pulsed through the sample (I). Contact with the sample was provided by the water-cooled electrodes (E, E') and the tungsten electrodes (F, F'). The graphite shields (G, G'), located on the tungsten electrodes, served to reduce end-radiation losses and acted as an alignment guide for the sample.

The d-c through the specimen caused a constant power to be dissipated uniformly throughout the sample volume. If no significant amount of heat were lost or measurements were made before such losses became sizable, the temperature of any sample region increased linearly with time. The specific heat at constant pressure, C_p°, could then be computed from the current, I, through the specimen, the potential drop, E, across a uniformly heated region of mass, m, and the rate of temperature increase as a function of time, dT/dt. The relationship between these quantities and C_p° is given by equation (253),



A	DC POWER SUPPLY	H-H'	POTENTIAL PROBES-TUNGSTEN
B	RECORDING OPTICAL PYROMETER	I	SPECIMEN
C	MICRO-OPTICAL PYROMETER	J	SPECIMEN SLOT
D	SIX CHANNEL RECORDER-DYNAGRAPH	K	FURNACE HEATER-GRAPHITE
E-E'	DC ELECTRODES-COPPER	L	RADIATION SHIELD-GRAPHITE
F-F'	ELECTRODE EXTENSION-TUNGSTEN	M	AC POWER SUPPLY
G-G'	RADIATION SHIELDS-GRAPHITE		

Figure 13 HIGH-TEMPERATURE SPECIFIC HEAT APPARATUS

$$C_p^o = \frac{EI}{Jm\,(dT/dt)} \quad , \qquad (253)$$

where J is the mechanical equivalent of heat.

The specimens, 1/2 inch in diameter and 4 inches in length, were slotted over a 2-inch center portion. The slots which were 1/16-inch wide and 1/4-inch deep extended the measurement time from less than 0.1 to 0.2 sec. This is due to the fact that the rate of rise of the specimen surface temperature was influenced sooner than the rate of rise of the center temperature by radiation losses to the heater element after a heat pulse.

The ambient temperature in the furnace was determined with a pyro-optical pyrometer, C, calibrated against NBS-calibrated tungsten-strip lamps, and corrected for the error introduced by an interposed quartz window. Periodical cross checks of the strip lamps were made with a gold melting-point apparatus. Typical pyrometer and quartz-window corrections are plotted in figure 14. Results of 20 pyrometer and lamp cross checks are summarized in Table LXXVIII. It can be seen that very little variation occurred in the calibration factor during the period of the project (1 year).

An optical pyrometer similar to that described by Rasor and McClelland[27] was used to record the temperature as a function of time on a Dynagraph recorder. The pyrometer used in this work employed a type 925 phototube with an S-1 spectral response. It was capable of response times of less than 0.01 sec. Calibration of this recording optical pyrometer, B in figure 13, was accomplished by comparison of a reading from a corrected, separate, micro-optical pyrometer with the phototube output recorded on a channel in the Offner Electronics Dynagraph recorder.

The determination of the rate of change of temperature as a function of time was done by means of equation (254),

$$\frac{de}{dt} \cdot \frac{ds}{de} \cdot \frac{dT}{ds} = \frac{dT}{dt} \quad , \qquad (254)$$

where

e = applied voltage

t = time

s = number of scale divisions

T = temperature.

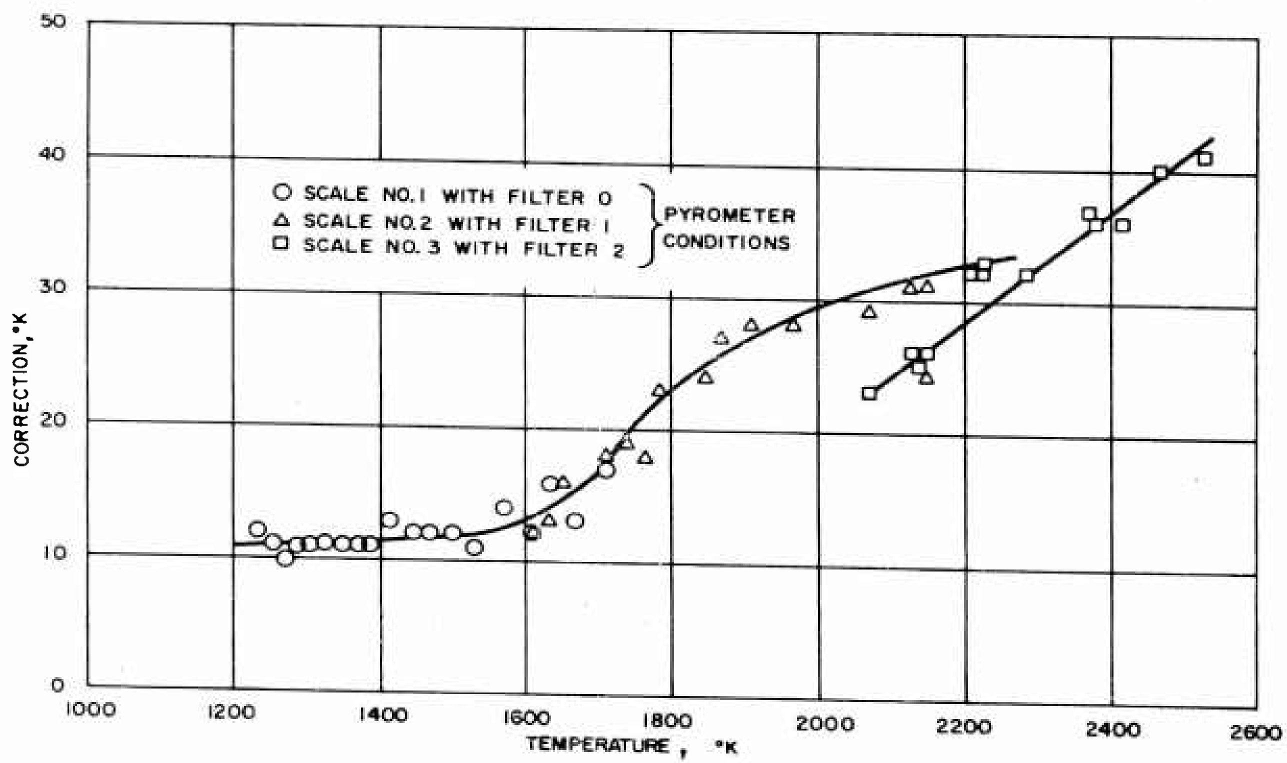


Figure 14 OPTICAL PYROMETER CORRECTION WITH ONE-EIGHTH INCH QUARTZ WINDOW

TABLE LXXVIII

PYRO-OPTICAL PYROMETER AND GOLD MELTING-POINT* (1336°K)

CROSS-CHECK DATA

Run No.	Corrected Pyrometer Reading °K	Thermocouple** Reading °K	Difference °K
1	1337	---	---
2	1335	1333	-2
3	1336	---	---
4	1335	1335	0
5	1334	1333	-1
6	1336	1335	-1
7	1332	1330	-2
8	1327	1333	+6
9	1330	1334	+4
10	1328	1332	+4
11	1337	---	---
12	1335	1333	-2
13	1336	---	---
14	1335	1335	0
15	1334	1333	-1
16	1336	1335	-1
17	1332	1330	-2
18	1327	1333	+6
19	1330	1334	+4
20	1328	1332	+4

* High-purity gold strip 1/6-inch wide x 0.005-inch thick.

** Platinum-platinum 10 percent rhodium, reference grade.

The first term on the left-hand side of equation (254) was obtained directly from the Dynagraph chart. The second term is a calibration term which was obtained by applying a known potential from a K-3 type potentiometer directly to the Dynagraph. The third term is the optical pyrometer calibration obtained as described above.

The potential drop, E, needed for equation (253) was obtained from the spring-loaded tungsten potential probes (H, H'). The current was determined from the potential drop across a high capacity shunt (2000 amperes maximum). Each of the needed quantities was recorded on a separate channel simultaneously.

The Dynagraph was well-suited for these measurements since it provided zero suppression in each channel, and only the deflections caused by the current pulse were recorded. Its reponse time of less than 1/120 sec and its chart speed of 25 cm/sec were alsc advantageous. Typical curves from Dynagraph records are illustrated in figure 15.

The specific heat values obtained by the techniques described were estimated to be accurate to within ± 5 percent.

4. Discussion of Results of High-Temperature Determinations

High-temperature specific heat determinations were completed with the pulse technique apparatus on four carbides, four borides, and one nitride. Average results at 2000°, 2300°, and 2500°K are summarized in Table LXXIX for purposes of discussion. These data were treated in the same way as those in Table II (section III-C5) of this report.

Most of the values are very large compared to the classical high-temperature limit of lattice harmonic vibration contributions (3R), but this is not unexpected. A few of the values are surprisingly high and still increasing with the temperature. These extremely large values are from samples of low purity (TiC and TiB_2). Because there is not enough past experience with data on these compounds at such high temperatures, it would be desirable to make a more detailed theoretical analysis, but that is not possible without the use of several other types of unavailable data in very complete form (refer to section III-C of this report for the applicable theoretical background).

For the reasons just-mentioned, it is important to subject high-temperature heat capacity data of this type to the test of comparison with the results of other workers. In the discussions that follow, the advantages of doing this will be evident. A number of positive checks support the general validity of the measurements made on this project. In the cases where there is not the required agreement, further work is required to find out the reasons which very likely will vary from one case to another.

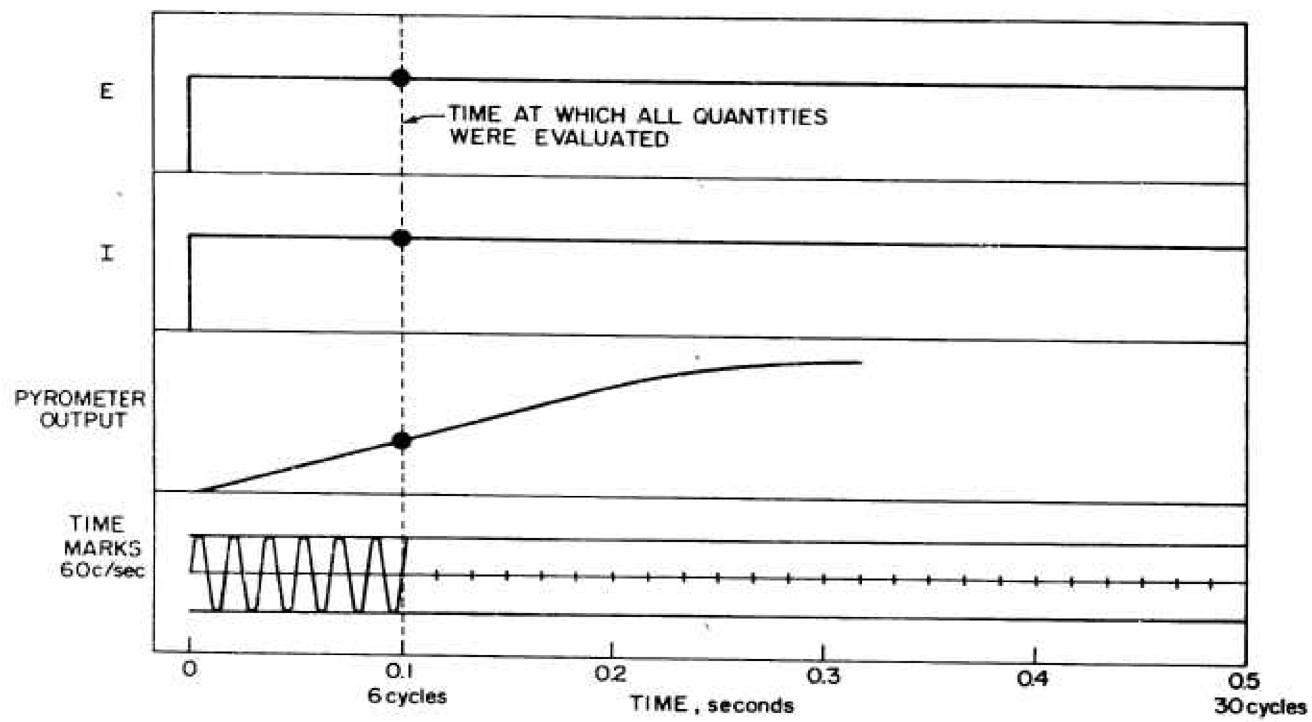


Figure 15 TYPICAL CURVES FROM DYNAGRAPH RECORDS

TABLE LXXIX

SUMMARY OF HIGH-TEMPERATURE SPECIFIC HEAT DATA AT THREE TEMPERATURES

Compound	No. of Atoms/gfw	Molecular Weight	Specific Heat in cal/^{o}K avg g atom		
			2000^{o}K	2300^{o}K	2500^{o}K
Carbides					
Niobium Carbide (NbC)	2	104.921	11.54	11.11	11.54
Tantalum Carbide (TaC)	2	192.961	6.75	9.17	9.26
Zirconium Carbide (ZrC)	2	103.231	10.38	10.38	10.38
Titanium Carbide (TiC)	2	59.911	14.68	16.87	18.27
Borides					
Zirconium Diboride (ZrB_2)	3	112.86	12.79	13.81	13.92
Tungsten Boride (WB)	2	194.68	10.61	11.10	11.78
Titanium Diboride (TiB_2)	3	69.54	11.75	14.81	16.74
Nitrides					
Titanium Nitride (TiN)	2	61.908	6.69	7.18	7.58
Graphite	1	12.011	5.89	5.89	6.02

One particularly important aspect of the work has been the verification of the purity of all test samples. This was done in pre-test analyses in nearly all cases. It resulted in the discontinuation of studies on the molybdenum boride sample because it was found to consist of four phases, Mo_2B, MoB, MoC, and Mo. A few post-test analyses were carried out to investigate any chemical or phase changes that might occur during the specific heat determinations.

a. Carbon

Carbon is a common element which has many uses in high-temperature technology in the form of graphite because of its extremely high melting point (in fact, it sublimes at one atmosphere without melting). Yet, its thermodynamic properties at high temperatures are still not known with any degree of assurance. Outstanding deficiencies in its available thermodynamic data are its equilibrium vapor species, the heats of vaporization of its vapor species, spectroscopic data for the vapor species other than C_2, and the specific heat of the solid at high temperatures. It was stated in section IV-A4a of this report that thermodynamic functions of graphite up to 6000°C could not be provided until better specific heat data became available. A review of the available data is therefore in order.

The available specific heat data for carbon are plotted in figure 16 for comparison purposes. Some of the additional points obtained on this project are given in Table LXXX and plotted in the figure also. The agreement between sets of data from different sources[27, 29, 173] is not very good except for that between the points from this project and the curve of Rasor and McClelland.[27] The sharp rise above 3000°C needs confirmation. Extrapolation to the sublimation point is obviously impossible.

b. Niobium Carbide (NbC)

The X-ray diffraction pattern of the niobium carbide specimen used in the specific heat determinations was that of NbC plus a weak pattern of Nb_2O_5. The results of the chemical analyses were as follows:

Element	Percent
Nb	86.66
Total C	10.81
Free C	<0.01

(continued on p. 1-354)

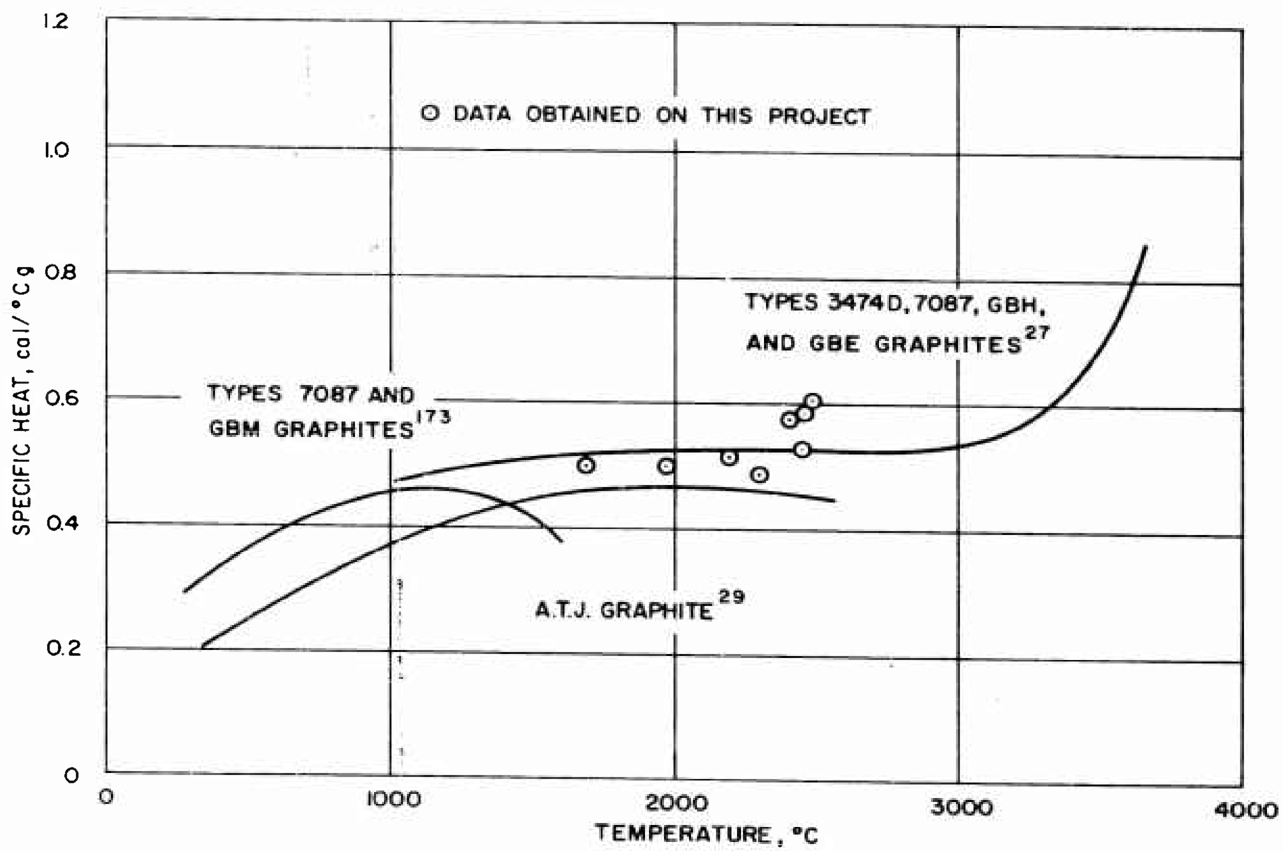


Figure 16 THE SPECIFIC HEAT OF CARBON VERSUS TEMPERATURE

TABLE LXXX

GRAPHITE HEAT CAPACITY

T, °K	cal/°K g	cal/°K g atom
1993	0.493	5.92
2188	0.526	6.32
2298	0.480	5.77
2429	0.570	6.85
2452	0.524	6.29
2461	0.588	7.06
2471	0.601	7.22
2483	0.448	5.38

(continued from p.1-351)

Element	Percent
Ta	1.82
Fe	0.06
Mg	0.0003
N	0.47, 0.46
O	0.22

Al, V, Ti, Zr, Ni, Mn, Hf, and Cr were not detected.

Since an unreported transition was discovered at ~ 2440°K and heat capacity values were high in the first series of specific heat measurements on NbC, the work was repeated with another sample to avoid any possibility of an accidentally wrong or impure sample. The temperature region in the vicinity of the transition point was extensively studied; several runs were made in both directions of increasing and decreasing temperature. Another purpose of repeated re-cycling of test runs was to detect any drift in specific heat with time due to reduction of the sample by the carbon vapor in the furnace.

The results are summarized in Table LXXXI and figures 17 and 18.

The transition was found to be completely reversible. A transition temperature of 2437°K was chosen. The nature of this transition remains to be clarified. The available information about the phase diagram of the Nb-C system[241, 490] provides no clues as to its nature since a broad homogeneity range exists at the stoichiometric composition. Other investigators[29] have not reported evidence for its existence, but the density of points in their work in the region of the transition temperature was not sufficient for this purpose.

The only available data from two sources are compared in figure 19. It is evident from this comparison that more experimental work will be required on the heat capacity of NbC.

c. Tantalum Carbide (TaC)

X-ray analysis of the tantalum carbide test specimen showed it to be a single phase of TaC. The results of the chemical analyses were as follows:

[490] Storms, E. K. and N. M. Krikorian, J. Phys. Chem. 64, 1471 (1960).

TABLE LXXXI

NIOBIUM CARBIDE (NbC) HEAT CAPACITY
(APPROXIMATELY 97.5 PERCENT PURITY)

Run	Temp	C_p°		Run	Temp	C_p°	
No.	°K	cal/°K g	cal/°K avg g atom	No.	°K	cal/°K g	cal/°K avg g atom
1	1763	0.151	7.92	3	2237	0.214	11.23
1	1817	0.163	8.55	5	2237	0.224	11.75
1	1840	0.178	9.34	2	2263	0.236	12.38
1	1868	0.221	11.60	5	2265	0.210	11.02
4	1952	0.210	11.02	7	2265	0.269	14.11
1	1961	0.208	10.91	3	2278	0.209	10.97
3	1970	0.230	12.07	2	2286	0.259	13.59
1	1971	0.225	11.81	4	2293	0.241	12.64
1	1983	0.225	11.81	2	2298	0.245	12.85
1	2051	0.220	11.54	5	2301	0.200	10.49
4	2053	0.237	12.43	3	2308	0.199	10.44
1	2068	0.234	12.28	2	2339	0.236	12.38
1	2077	0.232	12.17	5	2342	0.233	12.23
5	2091	0.202	10.60	2	2345	0.208	10.91
1	2095	0.234	12.28	3	2346	0.204	10.70
3	2115	0.236	12.38	4	2351	0.199	10.44
1	2141	0.219	11.49	6	2360	0.238	12.49
1	2146	0.231	12.12	6	2367	0.236	12.38
5	2154	0.210	11.02	3	2376	0.188	9.86
4	2154	0.216	11.33	5	2376	0.220	11.54
1	2158	0.241	12.64	5	2409	0.230	12.07
2	2193	0.203	10.65	4	2414	0.222	11.65
2	2199	0.245	12.85	2	2419	0.248	13.01
2	2206	0.270	14.17	3	2421	0.266	13.96

TABLE LXXXI (Concl'd)

Run No.	Temp °K	C_p° cal/°K g	C_p° cal/°K avg g atom
7	2421	0.273	14.32
2	2425	0.259	13.59
5	2440	0.290	15.22
3	2451	0.258	13.54
5	2453	0.268	14.06
7	2457	0.286	15.01
6	2464	0.240	12.59
3	2471	0.206	10.81
4	2475	0.228	11.96
2	2475	0.206	10.81
2	2477	0.209	10.97
2	2488	0.223	11.70
2	2494	0.233	12.23
2	2506	0.236	12.38
3	2507	0.221	11.60
2	2515	0.213	11.18
6	2518	0.235	12.33
3	2529	0.224	11.75

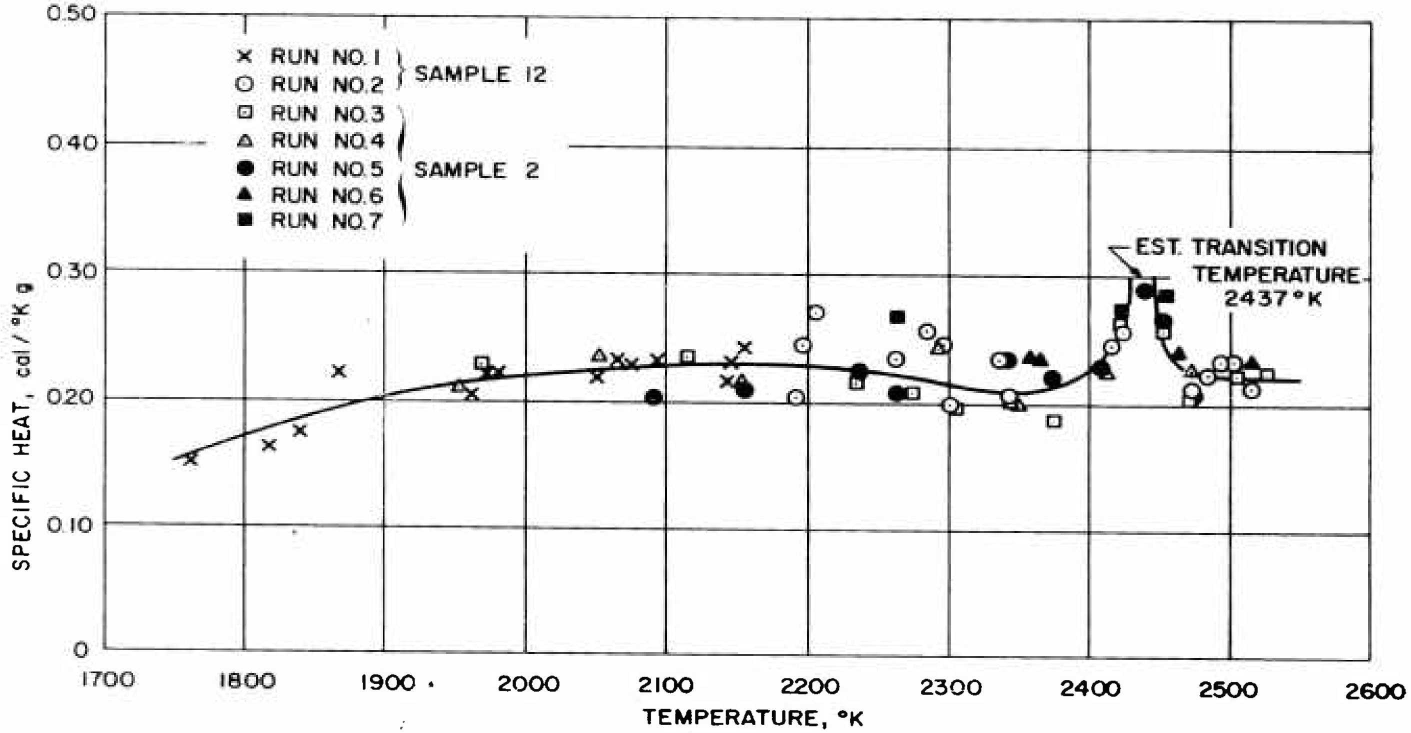


Figure 17 SPECIFIC HEAT OF NIOBIUM CARBIDE VERSUS TEMPERATURE

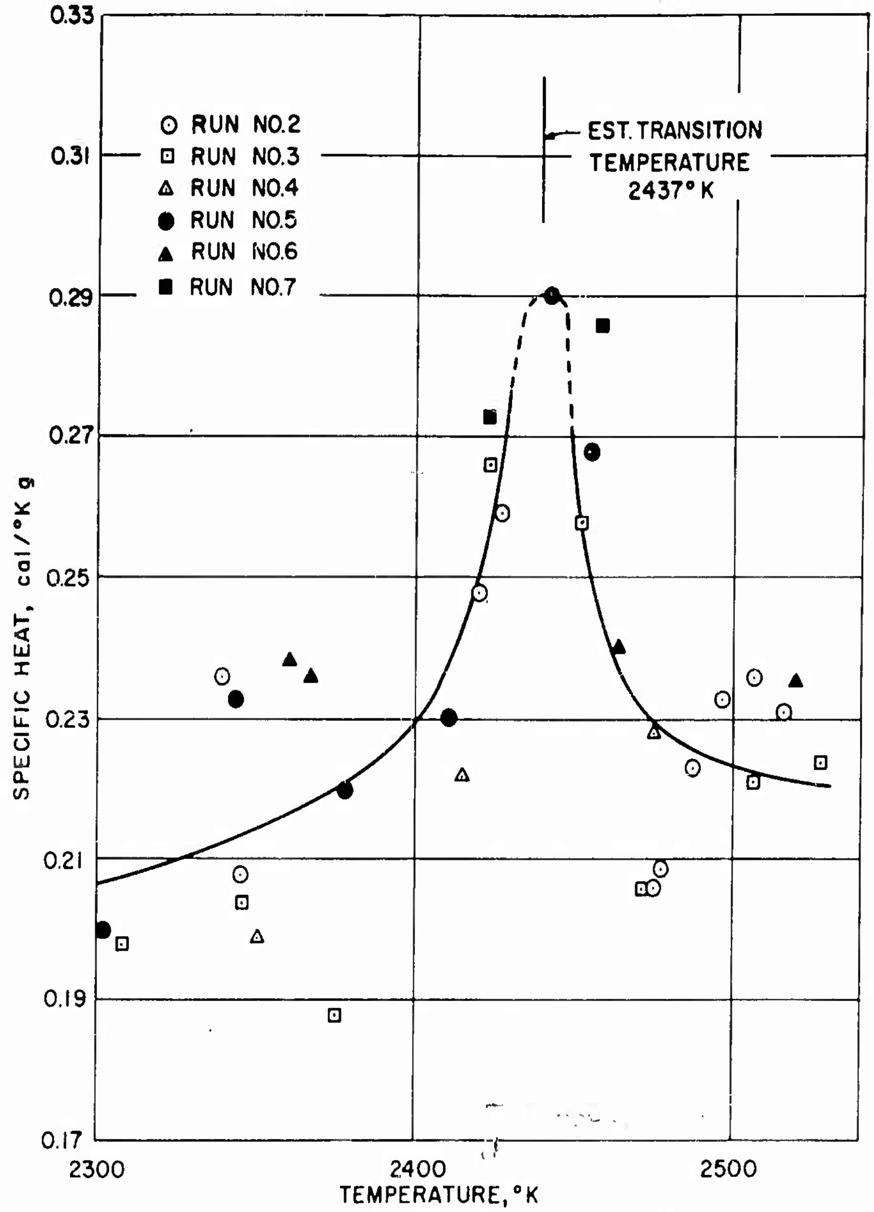


Figure 18 DETAILS OF REVERSIBLE TRANSITION IN NIOBIUM CARBIDE

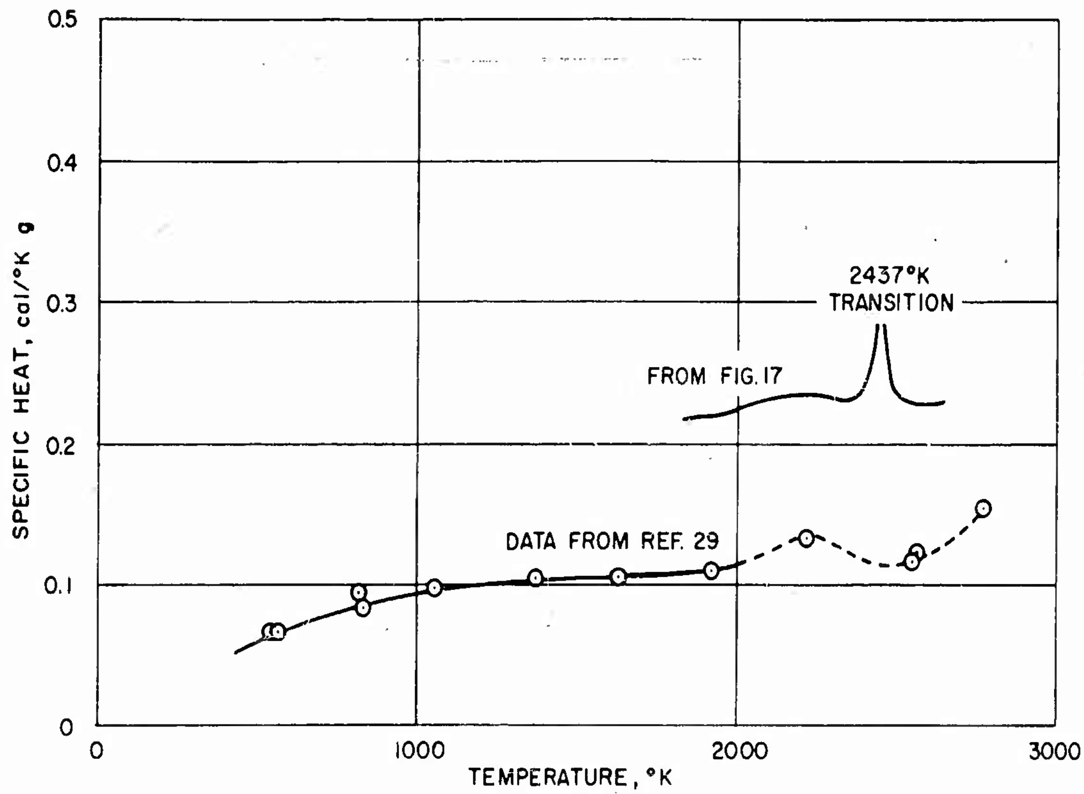


Figure 19 COMPARISON OF NIOBIUM CARBIDE SPECIFIC HEATS

Element	Percent
Total C	6.27 Avg.
Free C	0.04
O	0.18 Avg.
Ta	90.48
Ti	0.90
Fe	0.20
Mn	0.07
Hf	0.22
Nb	1.62
Zr	0.17
Cu	<0.01
Cr	<0.01
Ni	<0.01
N	0.09

The results of the high-temperature specific heat measurements are summarized in Table LXXXII and figure 20. A comparison of data from all sources is made in figure 21. The Southern Research Institute data[29] appear to have the best overall temperature dependence, but their general level appears to be slightly low in comparison with that of the other two sets of data.

Better agreement between the TaC specific heat data from various sources[29, 491] would be desirable for the preparation of thermodynamic tables. Further measurements were being made on a second specimen at the time of report writing to help resolve these discrepancies.

[491] Margrave, J.L. Private Communication (21 March 1961).

TABLE LXXXII

TANTALUM CARBIDE (TaC) HEAT CAPACITY
(APPROXIMATELY 96.7 PERCENT PURITY)

Temp	C_p^o		Temp	C_p^o	
°K	cal/°K g	cal/°K avg g atom	°K	cal/°K g	cal/°K avg g atom
1763	0.0691	5.98	2321	0.0922	7.97
1780	0.0786	6.80	2349	0.0888	7.68
1789	0.0800	6.92	2360	0.0908	7.85
1804	0.0855	7.39	2379	0.0892	7.71
1939	0.0693	5.99	2396	0.0935	8.09
1997	0.0945	8.17	2401	0.0966	8.35
2023	0.0710	6.14	2406	0.0845	7.31
2052	0.0822	7.11	2408	0.1027	8.88
2058	0.0793	6.86	2426	0.0831	7.19
2068	0.0857	7.41	2433	0.0917	7.93
2076	0.0832	7.20	2448	0.0837	7.24
2078	0.0953	8.24	2448	0.1086	9.39
2115	0.0768	6.64	2455	0.1080	9.34
2125	0.1011	8.74	2460	0.0858	7.42
2132	0.0791	6.84	2460	0.0972	8.41
2188	0.1054	9.12	2465	0.1065	9.21
2234	0.0833	7.20	2472	0.0728	6.30
2258	0.0824	7.13	2474	0.1090	9.43
2291	0.0905	7.83	2474	0.0958	8.29
2297	0.1065	9.21	2507	0.0878	7.59
2309	0.1070	9.25	2544	0.0782	6.76
2316	0.0946	8.18			

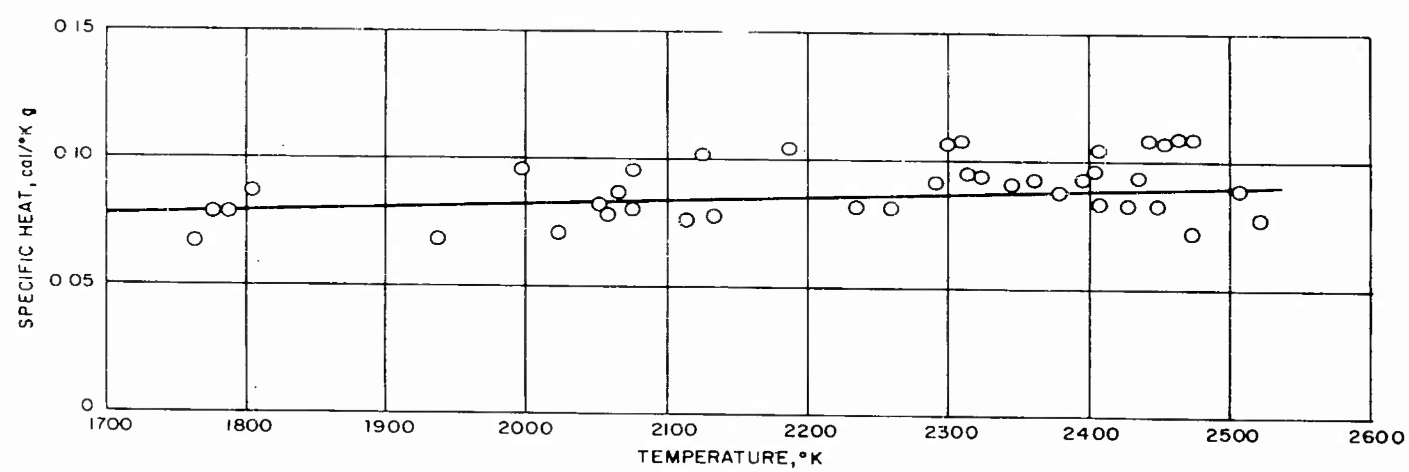


Figure 20 SPECIFIC HEAT OF TANTALUM CARBIDE VERSUS TEMPERATURE

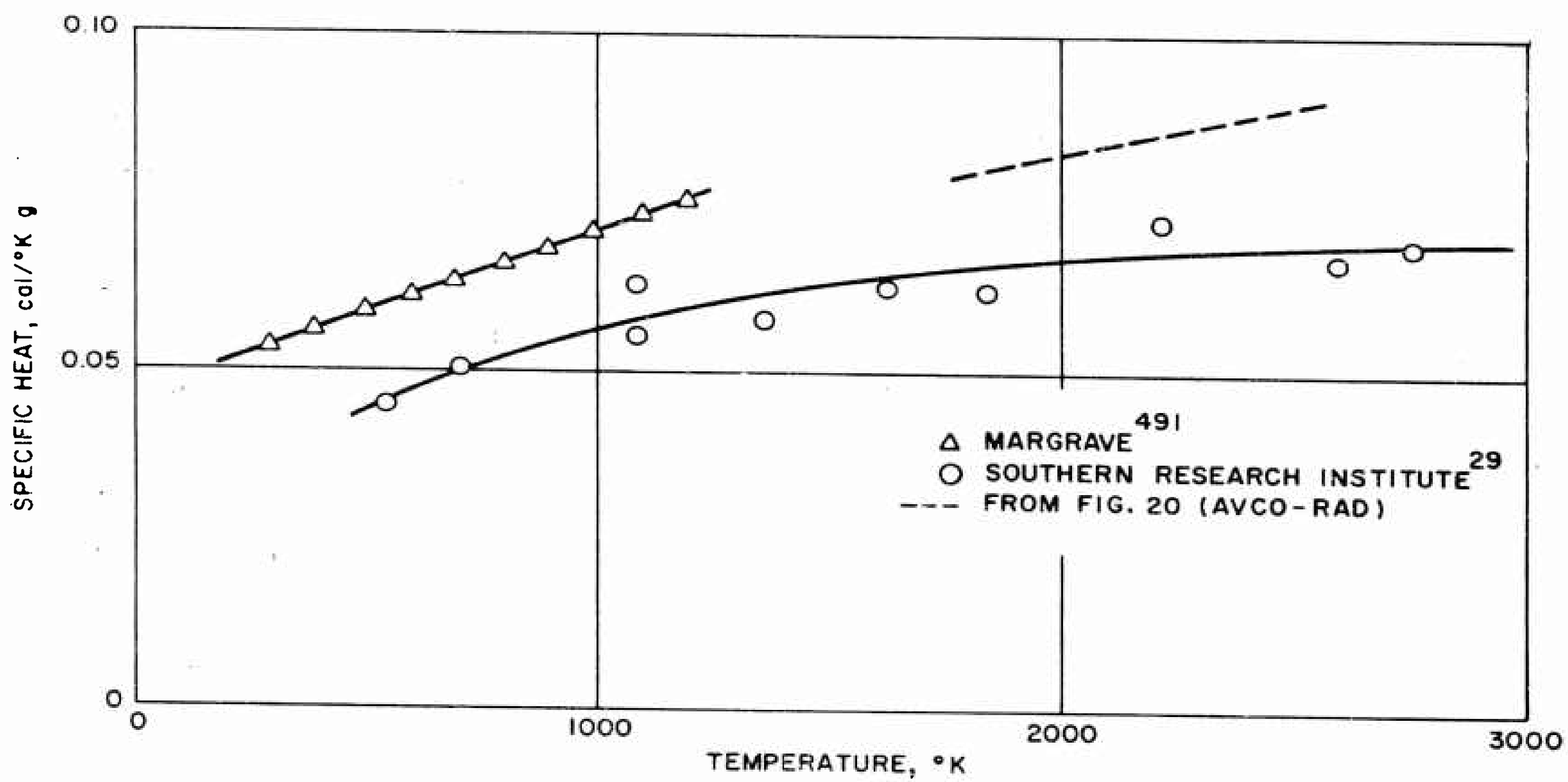


Figure 21 COMPARISON OF TANTALUM CARBIDE SPECIFIC HEATS

d. Titanium Diboride (TiB_2)

The X-ray diffraction diagram of the titanium diboride specimen was composed of a TiB_2 pattern and weak additional lines that were not identified. The following results of the chemical analyses showed that the specimen was only about 92 percent pure:

Element	Percent
O	0.77
C	1.24
B	26.61
Total Ti	64.90
Cu	0.005
Al	<0.1
Mn	----
Zr	0.51
Nb	0.09
Hf	<0.1
Fe	0.17
Cr	----
V	----
Mg	<0.001
Ni	----

Specific heat measurements were continued on the impure TiB_2 specimen since it was felt that corrections could be made later for the impurities and that the results would provide information on the effect of impurities on C_p° values at high temperatures. The results are summarized in Table LXXXIII and figure 22.

TABLE LXXXIII

TITANIUM DIBORIDE (TiB_2) HEAT CAPACITY
(Approximately 92 percent purity)

Temperature $^{\circ}K$	C_p° cal/$^{\circ}$K g	cal/$^{\circ}$K avg g atom
1733	0.384	8.28
1742	0.423	9.13
1746	0.388	8.39
1748	0.366	7.90
2006	0.542	11.78
2074	0.527	11.45
2077	0.559	12.15
2107	0.546	11.85
2152	0.541	11.73
2166	0.588	12.75
2172	0.581	12.59
2175	0.611	13.26
2203	0.604	13.10
2246	0.607	13.17
2310	0.675	14.65
2364	0.647	15.00
2396	0.680	15.76
2417	0.680	15.76

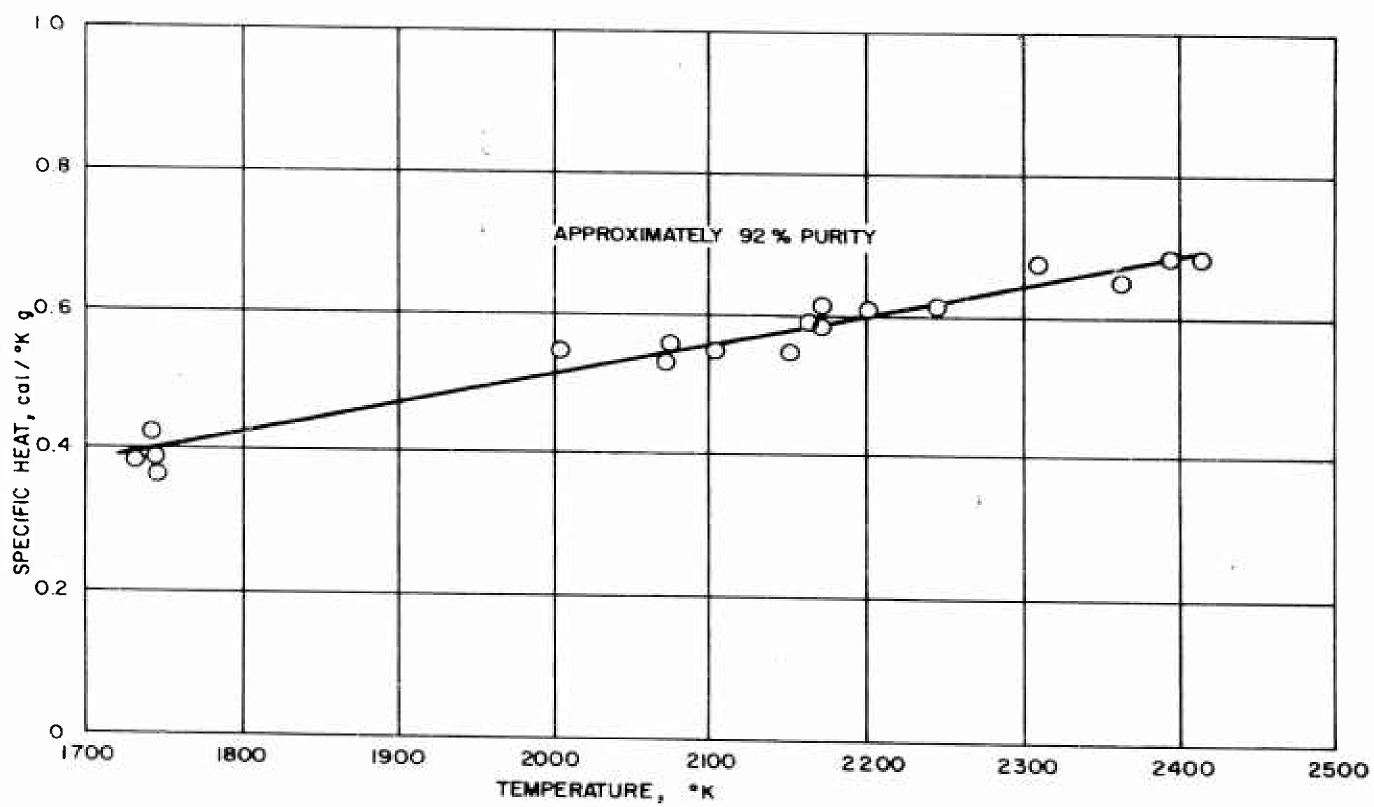


Figure 22 SPECIFIC HEAT OF TITANIUM DIBORIDE VERSUS TEMPERATURE

A comparison of these results with those of Margrave[491] (purity unspecified) is shown in figure 23. The specific heat of the impure specimen appears to be exceedingly high. Nothing else was found in the measurements to account for these high results. The surprisingly large apparent effect of the impurities in this specimen should be further investigated.

e. Titanium Carbide (TiC)

X-ray diffraction analysis of the titanium carbide specimen showed it to consist of a single phase of TiC. The following results of chemical analyses showed its purity to be approximately 95 percent:

Element	Percent
Cu	0.004
Al	<0.1
Mn	----
Zr	0.56
Nb	0.09
Hf	<0.1
Fe	0.12
Cr	----
V	----
Mg	<0.001
Ni	----
Total Ti	77.41
Free Ti	0.5
Total C	17.78
Free C	0.43

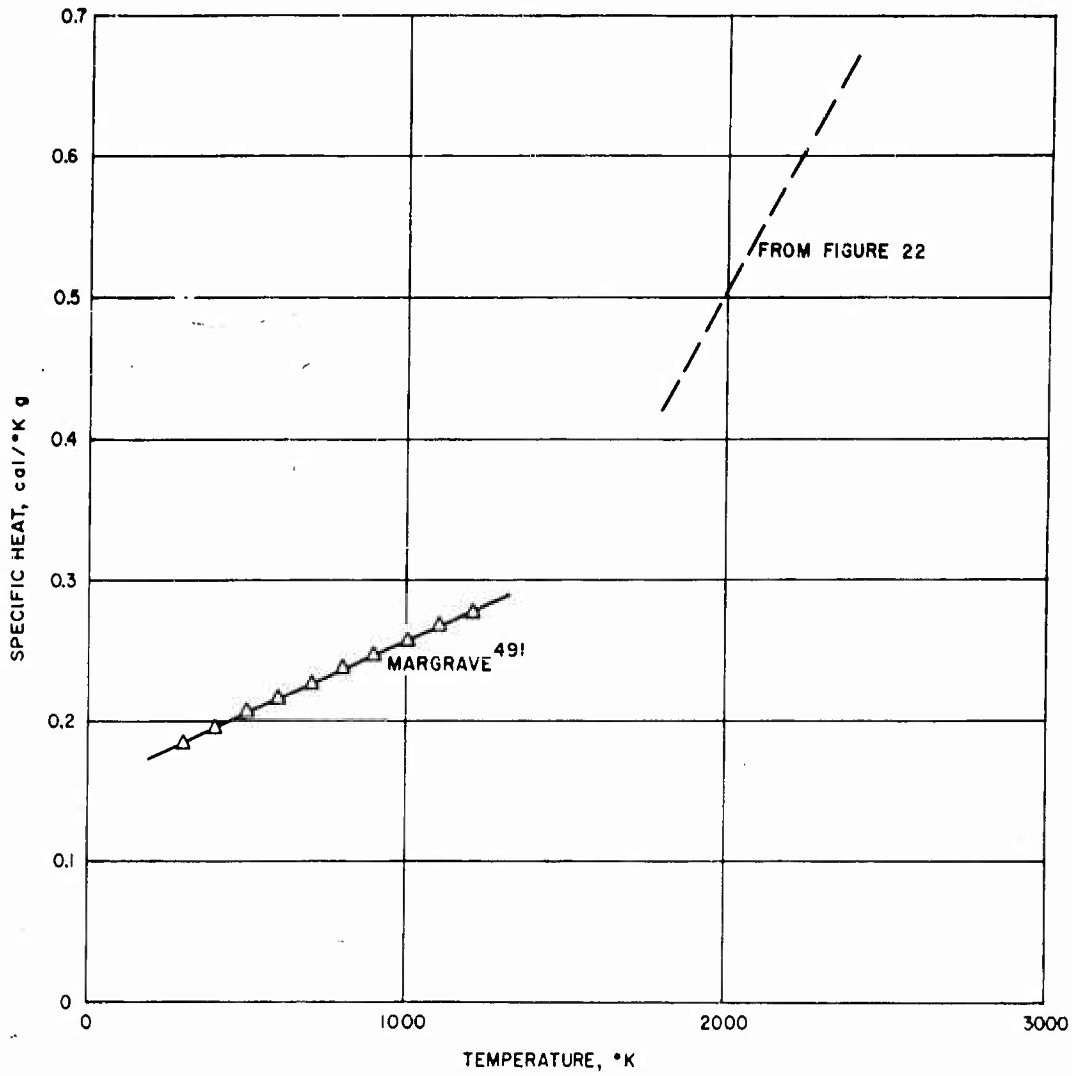


Figure 23 COMPARISON OF TITANIUM DIBORIDE SPECIFIC HEATS

The results of the specific heat measurements are summarized in Table LXXXIV and figure 24. Figure 25 shows a comparison of available specific heat data on TiC.[56, 464] The agreement between different sets of data is very poor. Impurities here again appear to have a large effect on both the level and slope of the specific heat versus temperature line obtained on this project.

f. Titanium Nitride (TiN)

The specific heat determinations on TiN were made in connection with another project wherein analytical data were not obtained. The results are reported here because of their importance to this project.

The results are summarized in Table LXXXV and figure 26. The data from various sources are compared in figure 27. The agreement between the sets of data is better in this case than in the others already considered. The purity of the TiN specimen used on this project was therefore probably satisfactory.

g. Tungsten Boride (WB)

X-ray diffraction analysis of the tungsten boride specimen revealed the existence of a single phase of WB. The following results of the chemical analyses showed that the sample purity was approximately 98.9 percent:

Element	Percent
W	93.7
B	5.16
C	0.09
O	0.16
N	0.01
Impurities	~0.88

The results of the specific heat determinations are summarized in Table LXXXVI and figure 28. The values in units of cal/°K avg g atom seem reasonable for the temperature range covered.

TABLE LXXXIV

TITANIUM CARBIDE (TiC) HEAT CAPACITY

Temperature ^{o}K	C_p^o	
	cal/^{o}K g	cal/^{o}K avg g atom
2023	0.467	13.99
2113	0.535	16.03
2186	0.520	15.58
2279	0.564	16.90
2353	0.589	17.64
2449	0.604	18.09
2506	0.602	18.03
2412	0.476	13.99
2252	0.510	15.28
2121	0.559	16.75

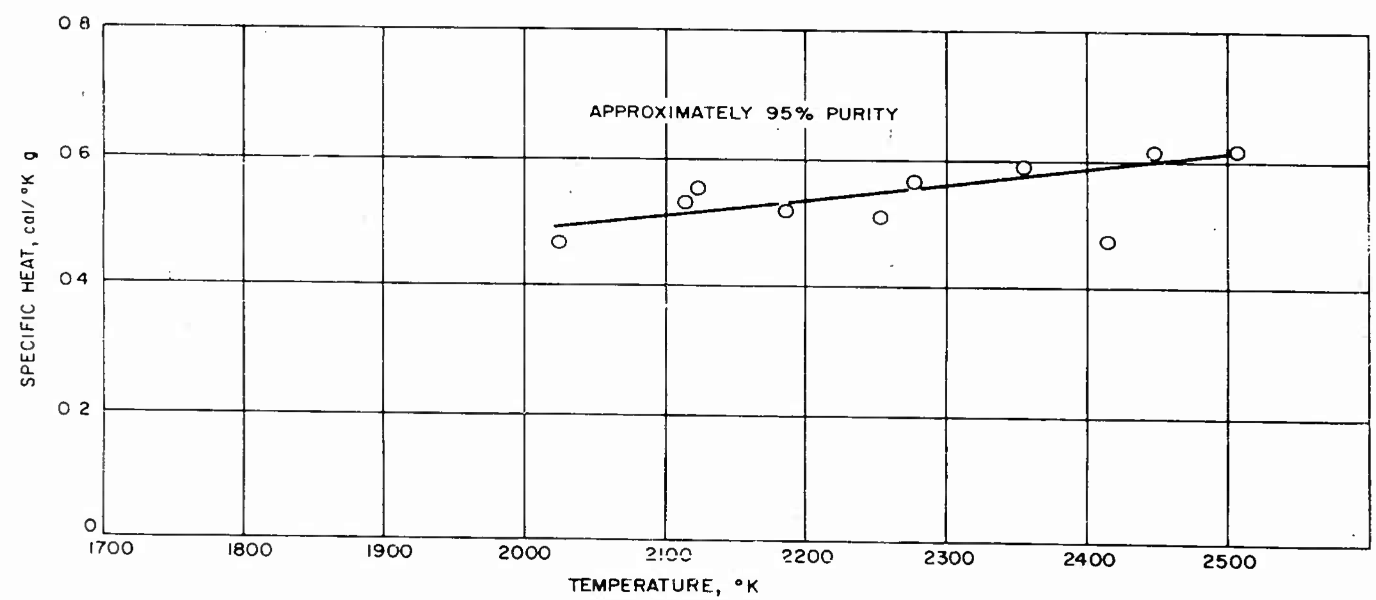


Figure 24 SPECIFIC HEAT OF TITANIUM CARBIDE VERSUS TEMPERATURE

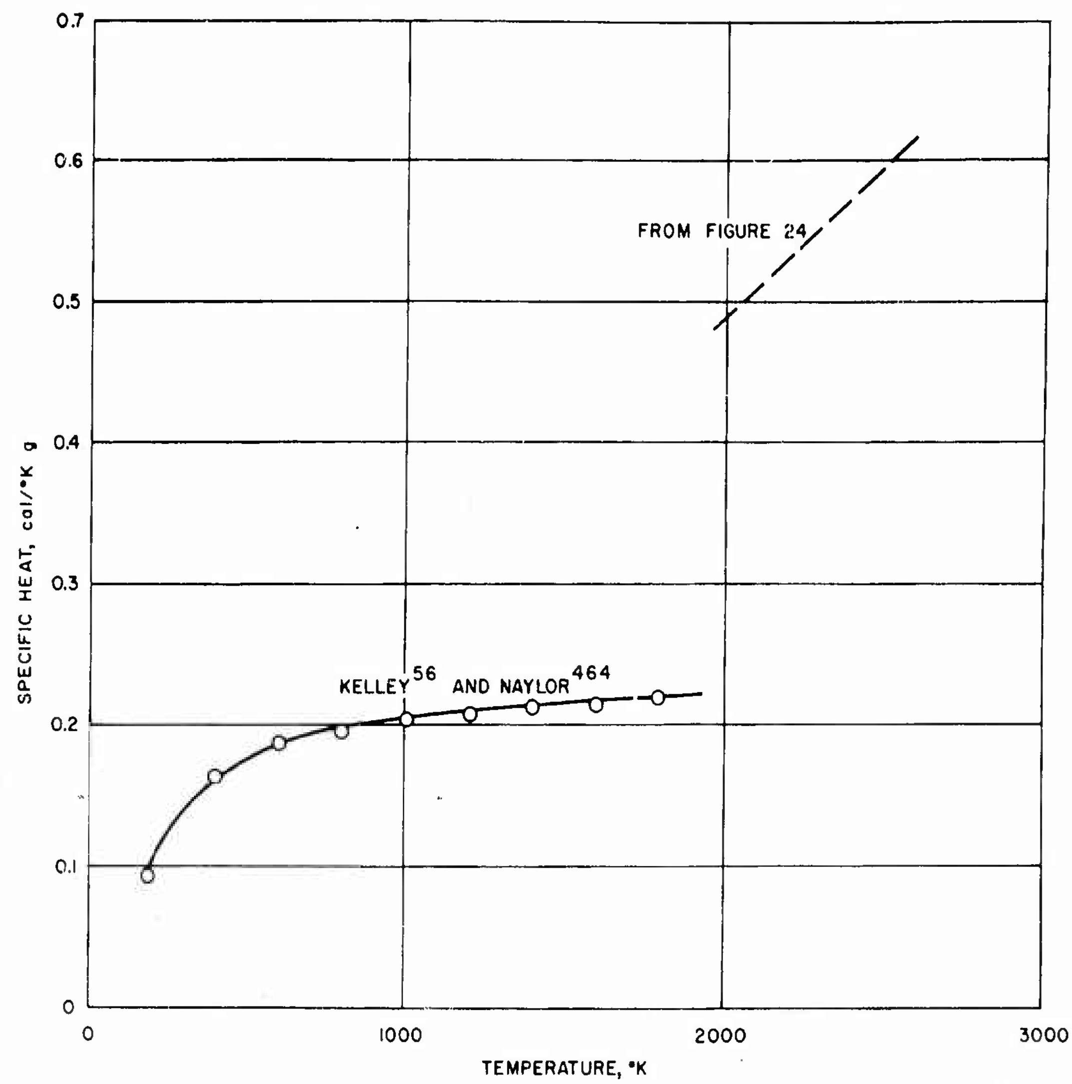


Figure 25 COMPARISON OF TITANIUM CARBIDE SPECIFIC HEATS

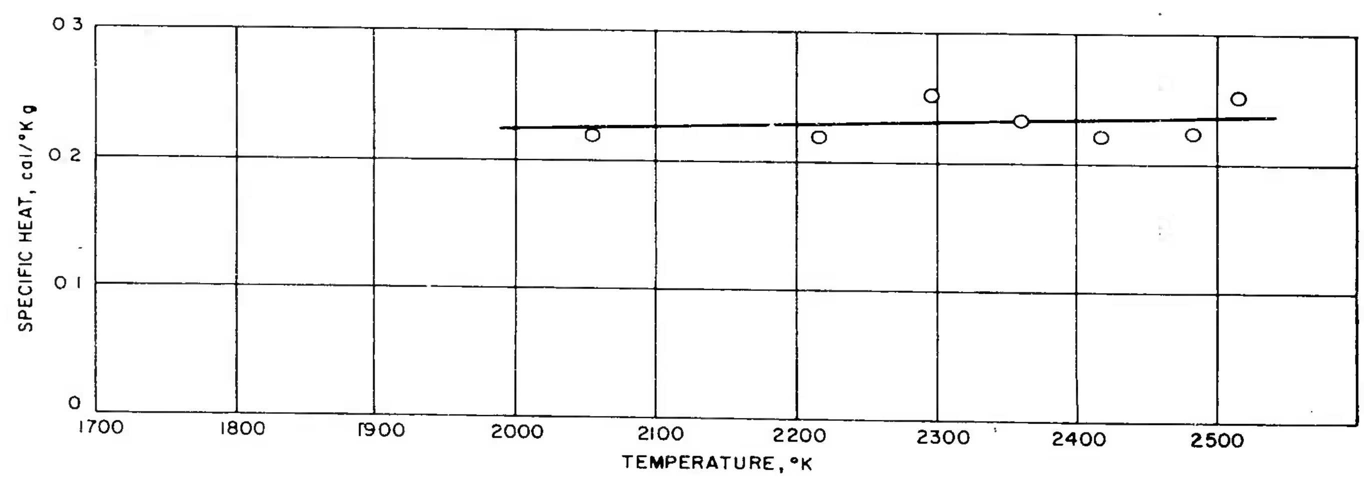


Figure 26 SPECIFIC HEAT OF TITANIUM NITRIDE VERSUS TEMPERATURE

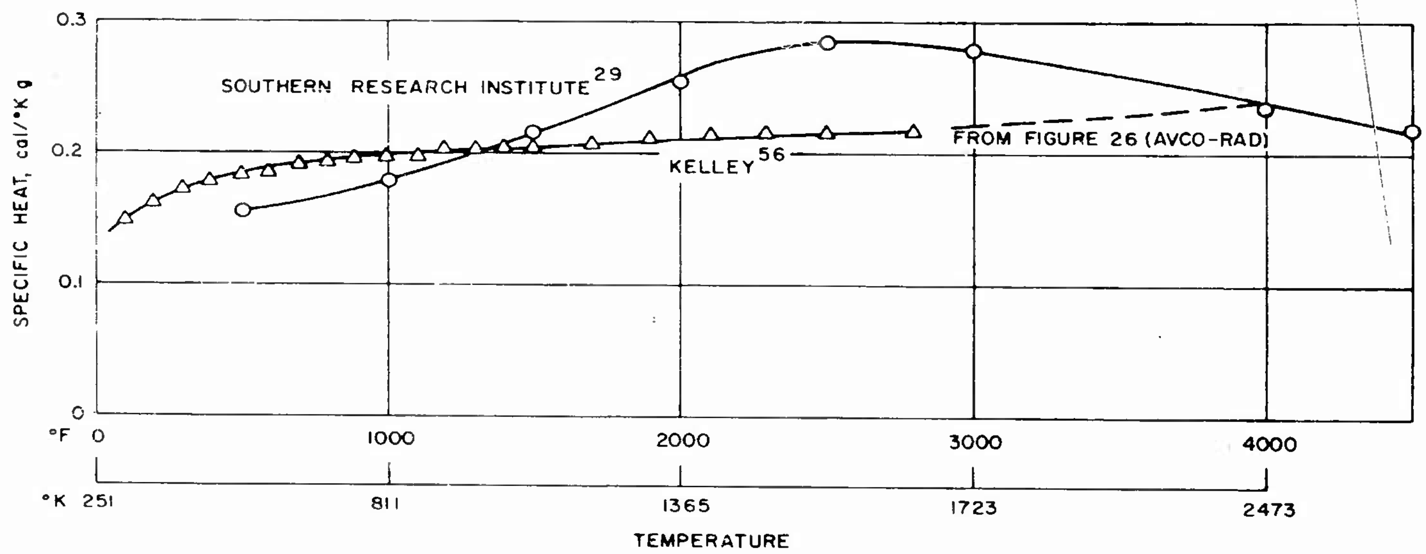


Figure 27 COMPARISON OF TITANIUM NITRIDE SPECIFIC HEATS

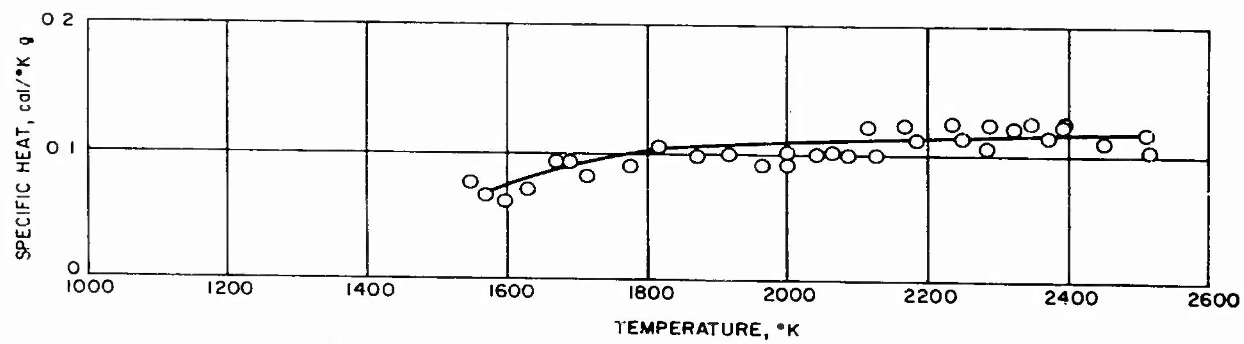


Figure 28 SPECIFIC HEAT OF TUNGSTEN BORIDE VERSUS TEMPERATURE

TABLE LXXXV

TITANIUM NITRIDE (TiN) HEAT CAPACITY

Temperature	C_p°	
$^\circ K$	cal/$^\circ$K g	cal/$^\circ$K avg g atom
2052	0.219	6.78
2217	0.220	6.81
2298	0.253	7.83
2360	0.234	7.24
2418	0.221	6.84
2482	0.223	6.90
2512	0.253	7.83

TABLE LXXXVI

TUNGSTEN BORIDE (WB) HEAT CAPACITY
(APPROXIMATELY 98.9 PERCENT PURITY)

Temp. °K	C_p^o cal/°K g	C_p^o cal/°K avg g atom	Temp. °K	C_p^o cal/°K g	C_p^o cal/°K avg g atom
1556	0.074	7.20	2118	0.121	11.78
1574	0.069	6.72	2129	0.101	9.83
1597	0.065	6.33	2169	0.123	11.97
1630	0.076	7.40	2192	0.114	11.10
1674	0.091	8.86	2232	0.122	11.88
1688	0.091	8.86	2247	0.117	11.39
1718	0.085	8.27	2281	0.110	10.71
1775	0.091	8.86	2286	0.125	12.17
1819	0.108	10.51	2321	0.118	11.49
1868	0.102	9.93	2345	0.129	12.56
1920	0.101	9.83	2379	0.118	11.49
1961	0.094	9.15	2393	0.123	11.97
2000	0.107	10.42	2399	0.125	12.17
2000	0.100	9.73	2458	0.116	11.29
2057	0.104	10.12	2518	0.109	10.61
2074	0.107	10.42	2518	0.120	11.68
2086	0.102	9.93			

h. Zirconium Diboride (ZrB_2)

The X-ray diffraction diagram of the zirconium diboride specimen contained a pattern of hexagonal ZrB_2 plus a weak pattern of ZrC. The following results of the chemical analyses indicated a purity of approximately 95.8 percent:

Element	Percent
Zr	78.94
B	16.86
O	1.36
Total C	0.37
Hf	<0.25
Fe	0.18
Ti	0.14
Mg	<0.01
Cu	<0.05
Mn	<0.01
V	<0.2
Nb	<0.01
Ni	<0.5
Cr	<0.1
Al	<0.3
N	0.14

Results of the specific heat determinations are summarized in Table LXXXVII and figure 29.

Repeated runs on the same specimen of ZrB_2 revealed no drift in specific heat versus time. This was taken as evidence that the effect of reactions with the carbon vapor in the furnace was negligible.

TABLE LXXXVII

ZIRCONIUM DIBORIDE (ZrB_2) HEAT CAPACITY
(APPROXIMATELY 95.8 PERCENT PURITY)

Run	Temp.	C_p^o		Run	Temp.	C_p^o	
No.	°K	cal/°K g	cal/°K avg g atom	No.	°K	cal/°K g	cal/°K avg g atom
2	1739	0.183	6.88	1	2169	0.372	14.00
2	1742	0.200	7.52	1	2183	0.367	13.81
2	1745	0.255	9.59	3	2224	0.392	14.75
2	1749	0.205	7.71	3	2232	0.347	13.05
2D	1765	0.228	8.58	1	2253	0.345	12.98
2D	1776	0.279	10.50	1	2265	0.352	13.24
2D	1786	0.288	10.84	3	2298	0.375	14.11
2D	1786	0.242	9.10	3	2298	0.349	13.13
2	1852	0.333	12.53	3	2306	0.337	12.68
2	1856	0.315	11.85	1	2327	0.361	13.58
1	1909	0.304	11.44	1	2345	0.357	13.43
1	1914	0.298	11.21	3	2382	0.365	13.73
1	1929	0.339	12.75	3	2384	0.346	13.02
2	1961	0.355	13.36	1	2408	0.346	13.02
2	1966	0.330	12.42	1	2414	0.346	13.02
2	1974	0.326	12.26	3	2437	0.389	14.63
1	1983	0.359	13.51	3	2440	0.389	14.63
2	2097	0.311	11.70	3	2443	0.314	11.81
1	2100	0.358	13.47	3	2498	0.376	14.15
1	2115	0.372	14.00	3	2500	0.326	12.26
3	2121	0.339	12.75	3	2504	0.332	12.49
3	2127	0.344	12.94	3	2507	0.315	11.85
				1	2507	0.371	13.96
				1	2518	0.415	15.61
				1	2521	0.389	14.63

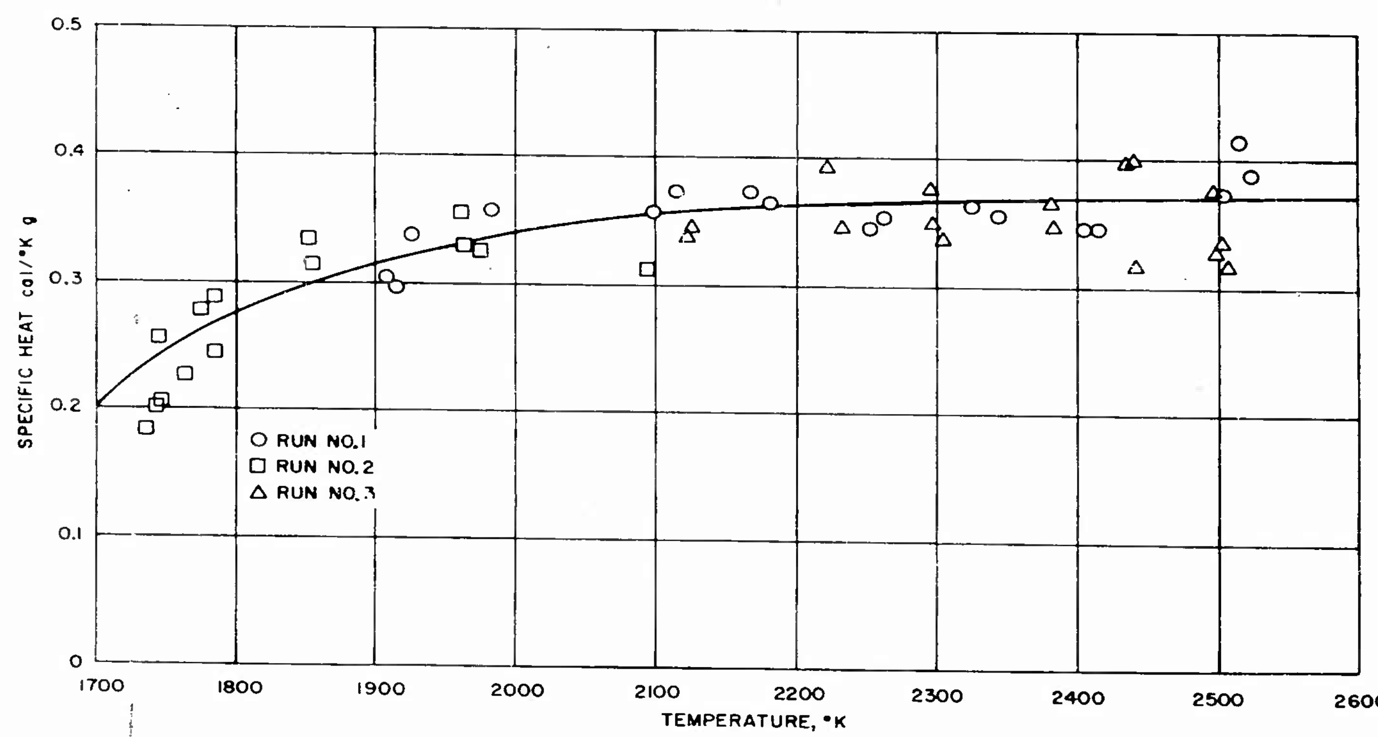


Figure 29 SPECIFIC HEAT OF ZIRCONIUM DIBORIDE VERSUS TEMPERATURE

i. Zirconium Carbide (ZrC)

The X-ray diffraction diagram of the ZrC specimen contained a pattern of ZrC plus a weak pattern of ZrB_2. The results of the following chemical analyses revealed the sample purity to be approximately 94.7 percent:

Element	Percent
Zr	84.23
O	1.21
Total C	10.46
Hf	0.78
Fe	0.19
Ti	0.14
Mg	<0.01
Cu	0.15
Mn	0.02
V	0.07
Nb	<0.3
Ni	<0.2
Cr	---
Al	0.12
Free C	0.25
N	1.03

Specific heat determinations were repeated several times in this case also in an attempt to detect any effect of the carbon vapor. No effect can be detected in the data which are summarized in Table LXXXVIII and figure 30. Specific heat data from various sources are compared in figure 31. Sample impurities (~4.3%) are probably again the cause of the high values in the figure 30 data.

TABLE LXXXVIII

ZIRCONIUM CARBIDE (ZrC) HEAT CAPACITY
(APPROXIMATELY 94.7 PERCENT PURITY)

Run	Temp.	C_p^o		Run	Temp.	C_p^o	
No.	°K	cal/°K g	cal/°K avg g atom	No.	°K	cal/°K g	cal/°K avg g atom
3	1639	0.204	10.53	2	2132	0.196	10.12
3	1648	0.171	8.83	3	2138	0.213	10.99
3	1675	0.225	11.61	1	2146	0.205	10.58
3	1696	0.187	9.65	3	2147	0.186	9.60
3	1721	0.200	10.32	3	2164	0.223	11.51
3	1799	0.193	9.96	4	2166	0.215	11.10
3	1814	0.195	10.07	3	2169	0.234	12.08
3	1897	0.221	11.41	4	2172	0.210	10.84
3	1915	0.196	10.12	3	2175	0.247	12.75
1	1955	0.206	10.63	1	2189	0.231	11.92
3	2017	0.182	9.39	1	2198	0.225	11.61
1	2023	0.204	10.53	2	2206	0.208	10.74
1	2057	0.204	10.53	4	2232	0.211	10.89
4	2071	0.208	10.74	4	2238	0.217	11.20
3	2080	0.202	10.43	1	2243	0.211	10.89
4	2080	0.208	10.74	2	2249	0.189	9.76
2	2085	0.208	10.74	2	2252	0.201	10.38
3	2094	0.189	9.76	4	2286	0.203	10.48
4	2094	0.213	10.99	1	2298	0.213	10.99
2	2100	0.221	11.41	4	2306	0.200	10.32
4	2107	0.232	11.98	2	2310	0.186	9.60
4	2113	0.224	11.56	4	2364	0.167	8.62
1	2113	0.224	11.56	1	2364	0.191	9.86
2	2118	0.210	10.84	4	2367	0.182	9.39

TABLE LXXXVIII (Concl'd)

Run No.	Temp. °K	C_p^o cal/°K g	C_p^o cal/°K avg g atom
1	2403	0.178	9.19
4	2411	0.176	9.08
4	2420	0.181	9.34
4	2471	0.180	9.29
4	2474	0.199	10.27
4	2483	0.187	9.65
4	2486	0.181	9.34
4	2492	0.196	10.12
4	2495	0.191	9.86
4	2499	0.196	10.12

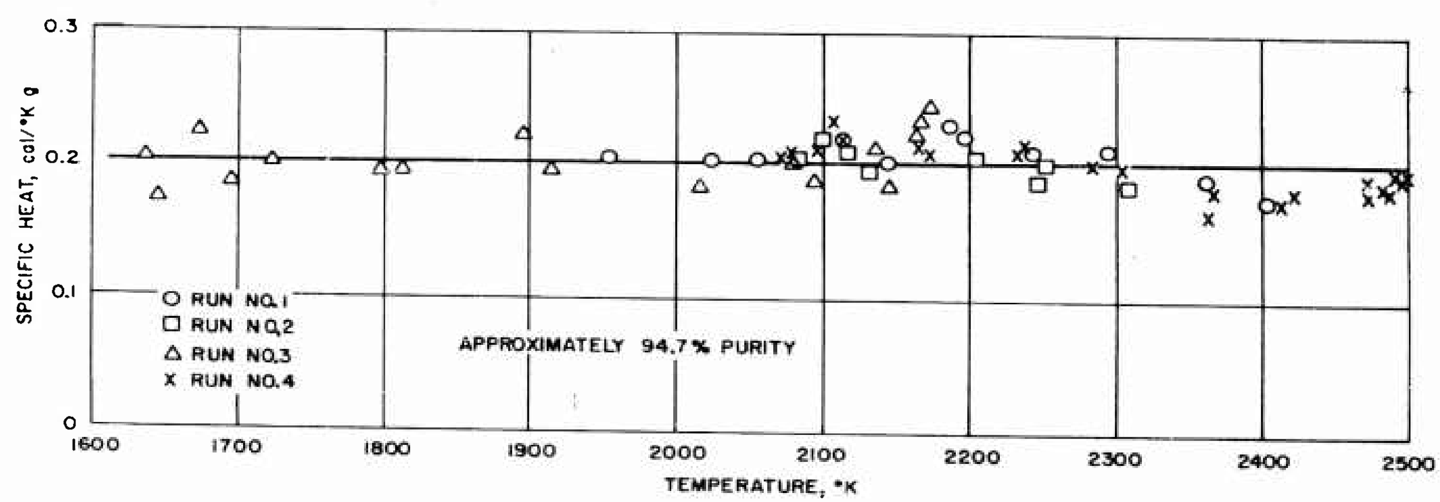


Figure 30 SPECIFIC HEAT OF ZIRCONIUM CARBIDE VERSUS TEMPERATURE

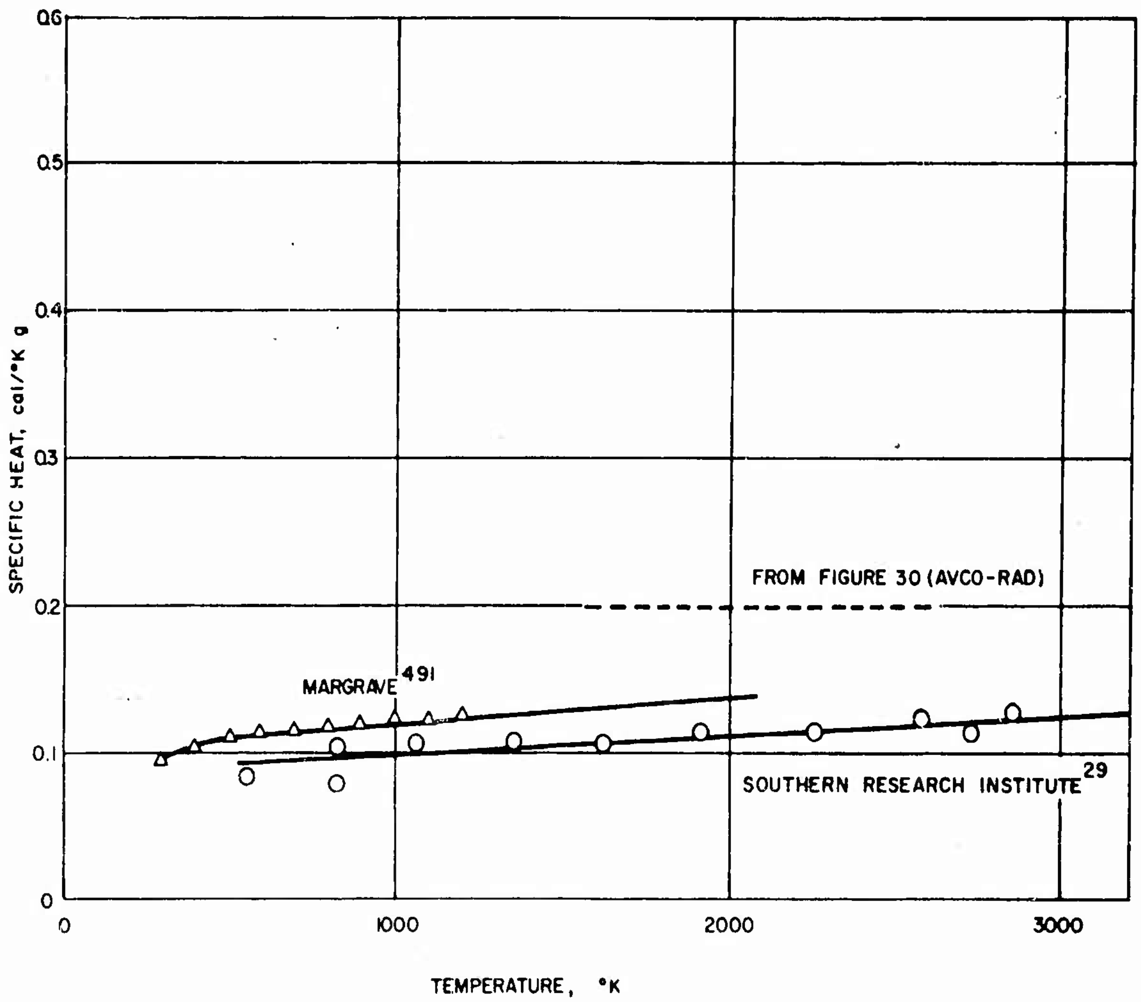


Figure 31 COMPARISON OF ZIRCONIUM CARBIDE SPECIFIC HEATS

C. SPECTROSCOPIC STUDIES

1. Introduction

Two important experimental techniques for the study of the vapors of refractory materials are as follows: (a) the vapor effusion technique with mass spectrometric identification of vapor species, and (b) the recording of the optical absorption or emission spectra of the vapors. These two techniques complement each other in that each provides needed data which the other cannot give.

The effusion-mass spectrometer technique, which has provided most of the published data, provides species identification and vapor pressures as a function of temperature of the various species in equilibrium with the condensed phase. From these quantitative data, one can calculate a number of thermodynamic properties, but a complete thermodynamic analysis requires the use of molecular parameters provided by optical spectroscopy.

Experiments utilizing optical spectroscopy can also be made to give quantitative data on the overall vapor-condensed phase equilibria, but usually not as easily and unambiguously as the effusion-mass spectrometer method. The great value of the optical spectroscopic technique is that it can give information on the intrinsic properties of the vapor species themselves. For example, the optical spectra yield molecular vibration frequencies which are needed for statistical mechanical calculations of free-energy functions, entropies, and enthalpies. Optical spectra also yield molecular configurations, force constants, bond strengths, and bond lengths, which are necessary for a basic understanding of chemical bonding and chemical reactions at high temperature. The latter parameters of similar compounds are often used to estimate vibration frequencies, moments of inertia, etc., for statistical mechanical calculations on species whose spectra have not been studied.

Part of the program of experimental studies in Phase III of this project was concerned with the determination of the molecular quantities just discussed for the vapor species in equilibrium with the solid phases of the refractory compounds included in the scope of the contract.

2. Experimental Technique

Absorption spectroscopy has been utilized in these studies of refractory compound vapors in preference to emission spectroscopy because it presents fewer basic experimental difficulties. The emission spectrum of a high-temperature vapor can be observed if the radiation emitted by the gaseous molecules can be distinguished from that scattered and emitted by hot particles condensed from the vapor. If condensation is successfully minimized or avoided, the use of a sensitive detection system will permit the emission spectrum to be observed over a short optical path. Unfortunately, it is experimentally difficult to avoid condensation in systems at very high temperature, and other measures must be taken to circumvent the problem. When an absorption spectrum is recorded, the problems presented by emitting and scattering condensate particles can be greatly reduced by modulation of the light from the source before passing it through the vapors. A tuned detection system can then discriminate the transmitted light from the light which originates in the hot zone. This does, however, require a relatively long optical path.

The present absorption work was performed with light paths of up to 200 feet through the hot vapors. Such long paths were achieved by the use of the White multiple reflection technique.[492] The absorption spectrum could be observed conveniently when the vapor pressure above the refractory sample was only a few microns. Being able to work at low vapor pressure presented a number of advantages, among which were the following:

a. Small quantities of material could be used and the sample was not lost rapidly.

b. It was not necessary to have inert gas present. Hence, convection currents were eliminated, and particle condensation was greatly reduced.

c. Reactions between the hot container and the material under study were usually not serious when the vapor pressure of the material was low.

d. Since convection currents were eliminated, it was not necessary to confine the vapors to a uniformly heated tube, and the refractory material could be evaporated from a hot filament, thus keeping power input and heat removal requirements down to a minimum.

A schematic diagram of the experimental apparatus is given in figure 32. Figure 33 is a photograph of the experimental apparatus (not including the power supply), and figure 34 shows some details of the interior of the reaction chamber. The entire heating, cooling, and optical assembly was mounted on an aluminum channel which slid out of the vacuum tank as shown in figure 34.

The heating element from which the material was evaporated consisted of a tungsten ribbon 0.004 inch thick, 1-1/2 inches wide, and 24 inches long. This ribbon was heated by the current from a bank of batteries and could reach temperatures above 3000°K. One end of the tungsten ribbon was connected directly to the electrically grounded channel. The other end went to

[492] White, J. N., J. Optical Soc. Am. 32, 285 (1942).

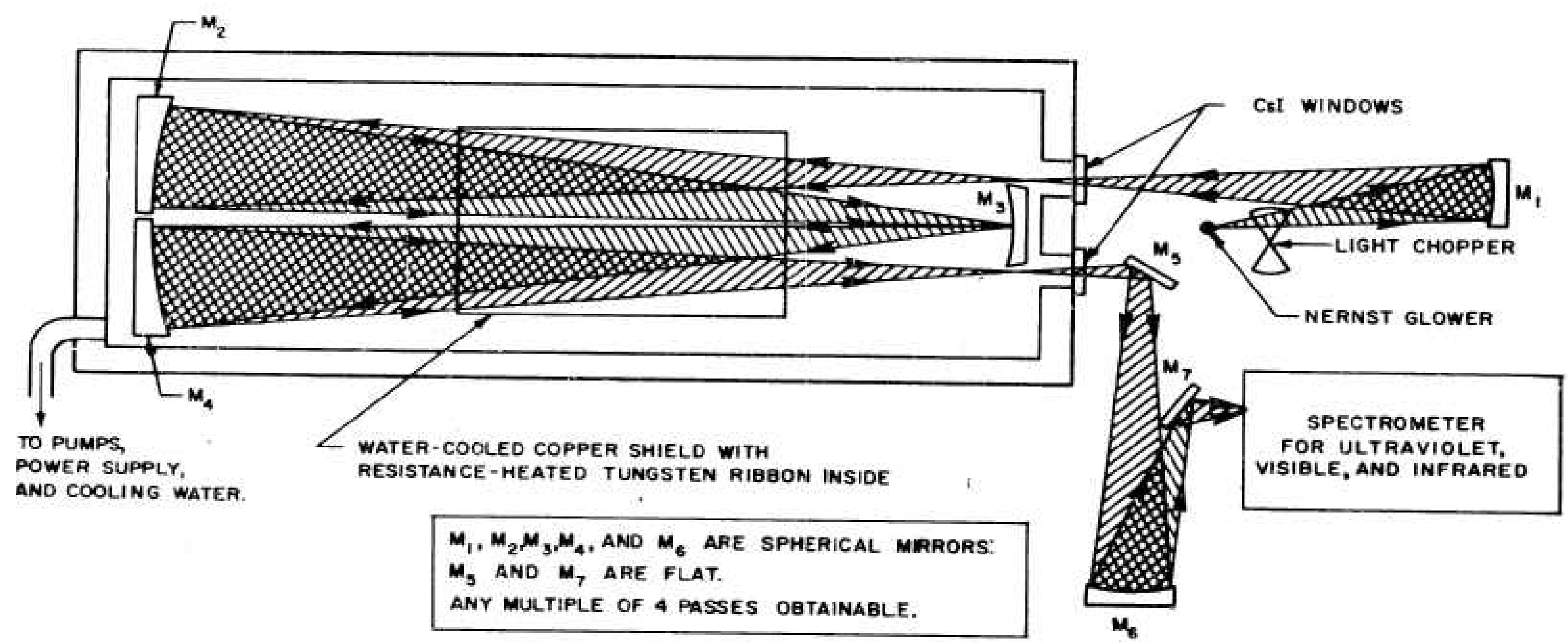
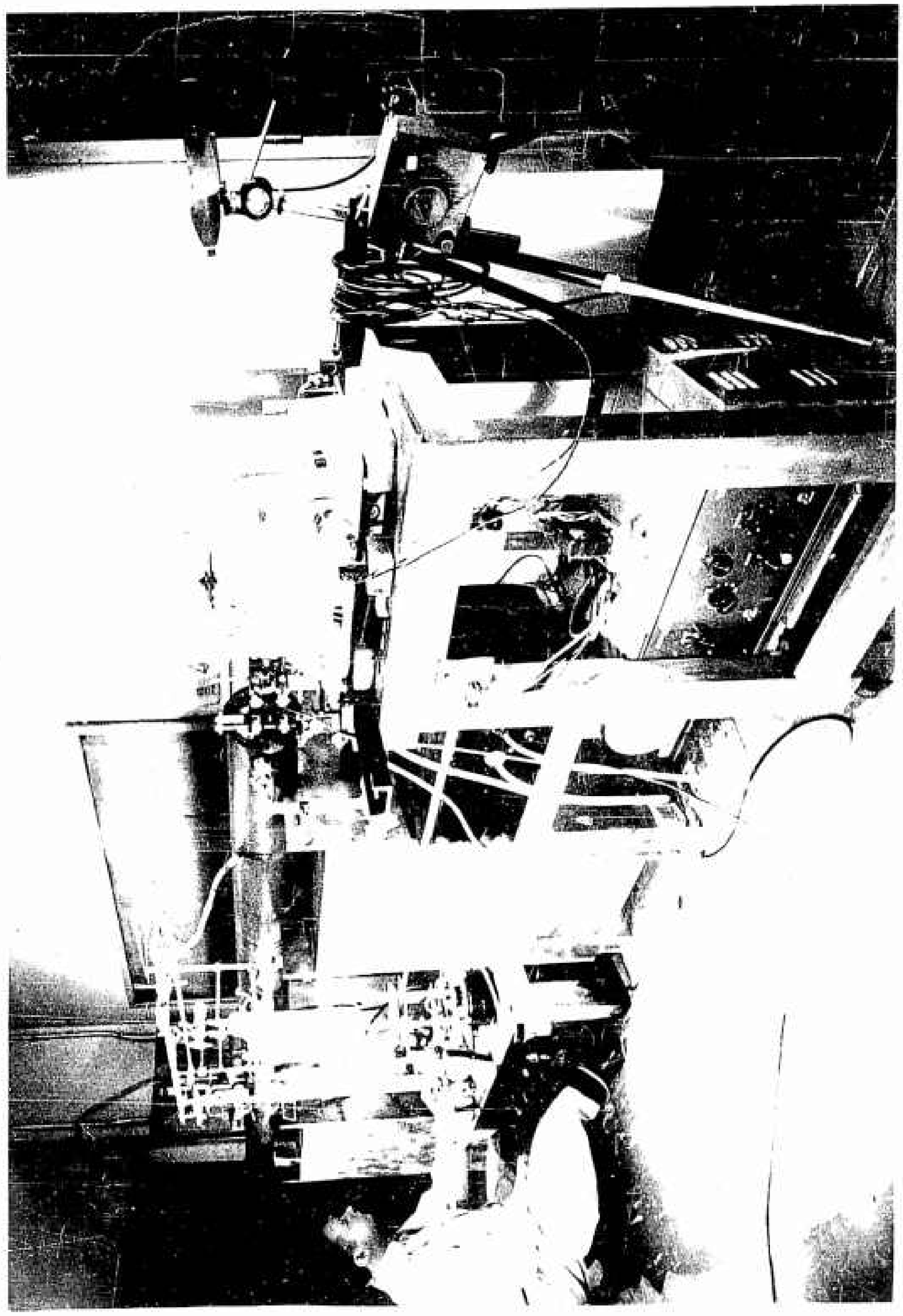
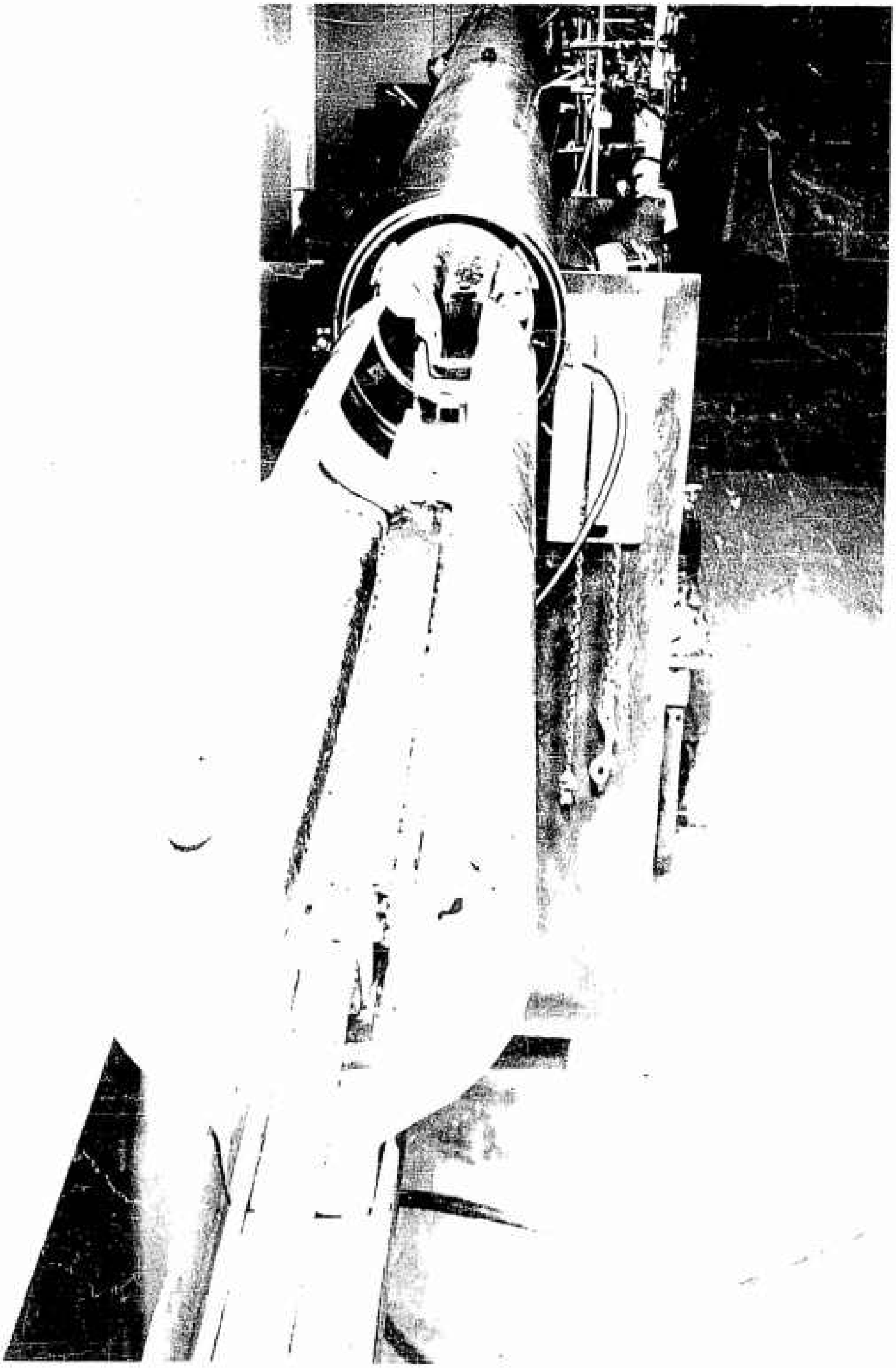


Figure 32 SCHEMATIC OF APPARATUS WITH FOLDED LIGHT PATH





the plus side of the batteries through a flexible cable which was spring-loaded to prevent the tungsten ribbon from going slack when it expanded on heating.

The heat radiated by the hot filament was removed from the interior of the vacuum tank by means of a water-cooled copper shield (shown in Fig. 34) which surrounded the sample. The heating element was sufficiently remote from the mirrors so that the latter did not heat up excessively or become coated with the condensed refractory vapor.

The vacuum chamber consisted of a steel pipe 8 inches in diameter and 11 feet long. The ends of the pipe were closed with Lucite discs in which were mounted KBr or CsI windows. It was evacuated by means of mechanical pumps to about 2 microns of pressure.

The spherical mirrors were aluminum-coated and had a 10-foot radius of curvature.

In operation, light from the Nernst glower source was projected into the White mirror system as a 4X-enlarged image; and, after being passed the desired number of times through the vapors, it was focused as a much-reduced image into the Perkin-Elmer monochromator. The number of light passes through the vacuum chamber depended on the angle between the mirrors paired at one end of the cell. When a total light path of 1000 feet was used (200 feet over the filament), the transmitted light was still detectable over the spectral region accessible with sodium chloride optics. The 13-cycle light modulation took place prior to traversal through the vapor. The tuned detection system responded only to light which had been passed through the vapors and not to unmodulated light emitted or scattered by hot particles or gases in the tank. By the use of various prisms and detectors, the spectral region from 0.2 and 40 microns could be covered.

A typical experiment was performed as follows:

1) The powdered refractory was sprinkled on the tungsten ribbon.

2) The carriage was pushed into the vacuum tank, water and power connections were made, and the optical system was adjusted for the desired number of traversals, which might be 100 or less.

3) The tank was evacuated to a pressure of 1 or 2 microns.

4) The desired current, usually between 200 and 500 amperes, heated the filament and slowly vaporized the refractory powder.

5) The absorption spectrum of the vapors was recorded while they were diffusing to and depositing on the water-cooled shield.

6) The filament temperature was read by sighting with an optical pyrometer through the Lucite disc at one end of the vacuum chamber.

3. Experimental Results

a. Silicon Carbide

Silicon, evaporated from a carbon filament, and silicon carbide, evaporated from a tungsten filament, both yielded the absorption spectrum shown in figure 35. The light path through the heated vapors was approximately 150 feet long.

According to Drowart et al the vapors in equilibrium with silicon carbide at 2200°K include approximately 5×10^{-6} atmosphere each of SiC_2 and Si_2C.[493] They are the most predominant species in the vapor, except for silicon atoms.

In the optical spectrum, there appeared to be one strong broad band centered at about 1080 cm^{-1} and two weaker bands centered at about 850 cm^{-1} and 600 cm^{-1}, respectively. The breadth of the bands was considerably greater than one is accustomed to seeing in absorption spectra at ordinary temperatures. This breadth may be attributed both to the spreading of the rotational structure due to the high temperature and to the superposition of "hot" bands on the fundamental band. It appears to be impossible to locate the band origin exactly. Therefore, the best that can be done is to choose the center of the band and to assign to it the corresponding vibrational frequency.[493]

Kleman has observed blue-green electronic emission bands, which he ascribed to SiC_2, and from an analysis of the spectrum, predicted infrared bands at 1742 and 591 cm^{-1}, but not at 1080 cm^{-1}.[494] It, therefore, seemed likely that the emitter of the 1080 cm^{-1} band was Si_2C. Drowart assumed Si_2C to be a linear asymmetric molecule, by analogy with SiC_2, and estimated its vibration frequencies to be $\omega_1 = 799$ cm^{-1}, $\omega_2 = 265$ cm^{-1}, and $\omega_3 = 446$ cm^{-1}. It appeared more likely, however, that the structure of the SiC_2 molecule was linear symmetric (Si-C-Si) because the magnitude of the vibrational force constants shows definitely that the Si-C bond is stronger than that of Si-Si (for Si-C, $k = 3.1 \times 10^5$ dynes per cm, and for Si-Si, $k = 2.1 \times 10^5$ dynes per cm).[493]

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[493] Drowart, J., G. DeMaria, and M. G. Inghram, J. Chem. Phys. 29, 1015 (1958).

[494] Kleman, B., Astrophys. J. 123, 162 (1956).

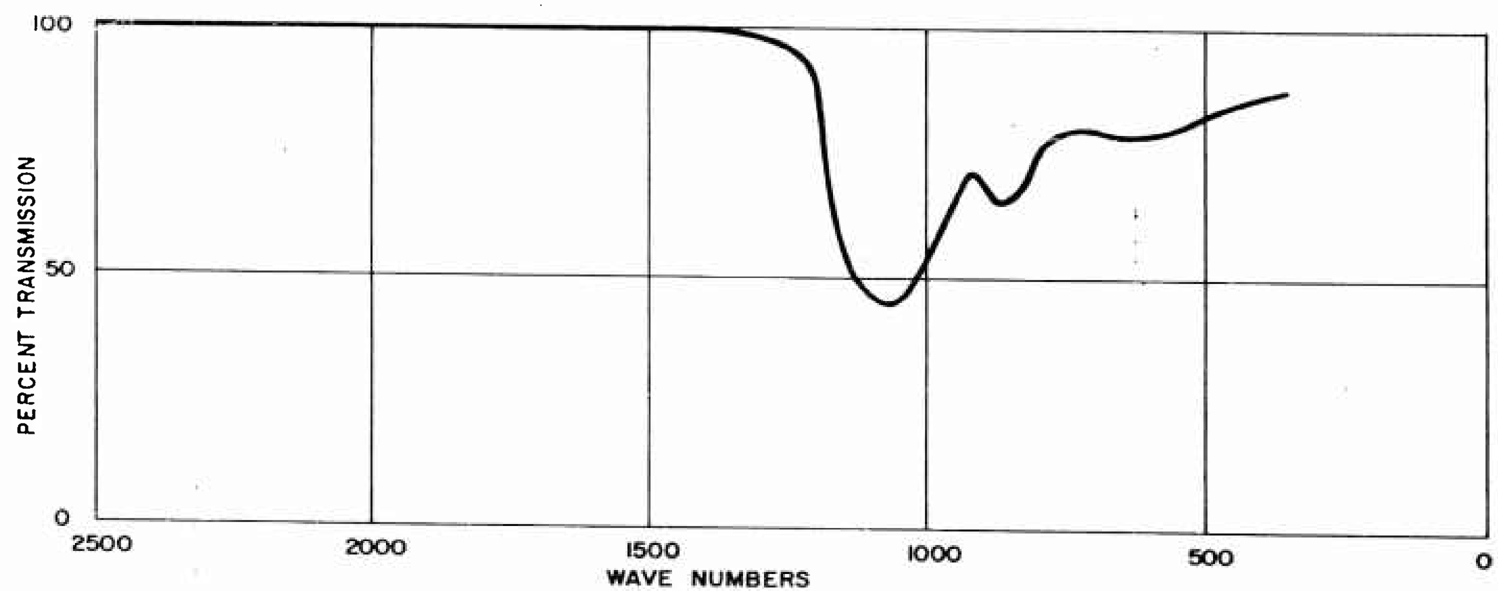

Figure 35 INFRARED ABSORPTION SPECTRUM OF VAPORS FROM A SILICON-CARBON SYSTEM HEATED TO 2200° K

The assumption that the structure is Si–C–Si permits the calculation of the force constants from the observed infrared spectrum.[400] Only the ω_3 band is expected to occur in the region from 2 to 15 microns. ω_1 is not infrared active because of symmetry considerations; and ω_2, the bending mode, will occur at longer wavelengths. The 1080 cm^{-1} band must therefore be associated with ω_3, and the corresponding force constant is $k = 3.4 \times 10^5$ dynes per cm. This value of k corresponds to the bond strength of the Si-C bonds in SiC_2, where $k = 2.9 \times 10^5$ dynes per cm, and to that in SiC, where $k = 3.1 \times 10^5$ dynes per cm. ω_1, associated with the symmetric stretching vibration, was calculated from k to be 447 cm^{-1}. If the bending force constant, k_δ, is similar to that measured for CO_2 and CS_2, or approximately 0.65×10^{-11} dyne-cm/rad, the doubly degenerate vibrational mode, ω_2, will occur at about 435 cm^{-1}. No particular band is evident at that frequency in figure 35. If the band exists, it must be very weak and is probably overlapped by the broad 591 cm^{-1} ω_1 band of SiC_2 which is perhaps discernible in the spectrum.

The somewhat narrower band which shows in the spectrum at 850 cm^{-1} may possibly be due to an impurity; it does not seem likely that it would be due to any species containing only silicon and carbon. Pure silicon was vaporized, and its spectrum was recorded to see whether this band might possibly be due to Si_3. This was found not to be the case. The silicon vapor showed no absorption bands in the region from 2 to 15 microns even at high partial pressure.

b. Molybdenum Trioxide

As stated in section IV-B5, there were no spectroscopic data reported for the gaseous species of molybdenum oxides. The properties of these oxides made them good candidates for study by the techniques described in section V-C2 above, and the investigation was undertaken.

The infrared absorption spectrum of the vapors from MoO_3 is shown in figure 36. It consists of one strong band centered at about 810 cm^{-1}. MoO_3 was reported[427, 417] to vaporize principally as the trimer, Mo_3O_9. A likely structure for this trimer appears to be a puckered, 6-membered ring of alternating molybdenum and oxygen atoms with the other 6 oxygen atoms doubly bonded to the molybdenum atoms, 3 above the ring and 3 below.

The vibrational pattern of such a large molecule is undoubtedly extremely complicated, but it can be expected to have as a predominant feature the stretching of the 6 Mo = O bonds. Hence, it seems reasonable to attribute the one strong band observed to the stretching vibration between oxygen and the rest of the molecule. This permits the calculation

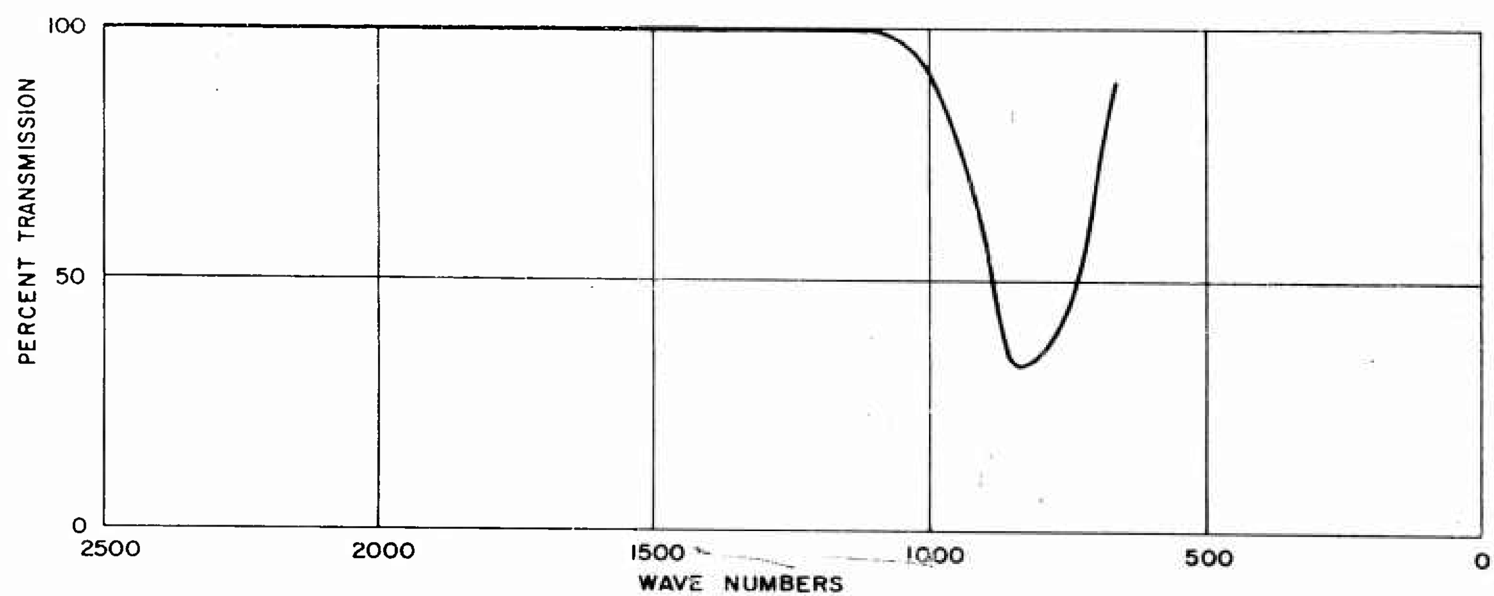

Figure 36 INFRARED ABSORPTION SPECTRUM OF VAPORS FROM MOLYBDENUM TRIOXIDE HEATED TO 1040° K

of the stretching force constant, k, from equation (255), where μ is the reduced mass, and ν the frequency.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad (255)$$

The value thus obtained is $k = 6.0 \times 10^5$ dynes/cm.

This value of k can then be used to calculate vibrational frequencies for the molecules MoO_2 and MoO_3 if the reasonable assumption is made that the Mo = O bonds in MoO_2, MoO_3, and Mo_3O_9 are similar. This calculation yields the values $\omega_1 = 794$ cm^{-1} and $\omega_3 = 915$ cm^{-1}, for a linear MoO_2 molecule. The estimated value of the k used in the calculation of section IV-B5b of this report would yield $\omega_1 = 778$ cm^{-1} and $\omega_3 = 898$ cm^{-1} for a linear MoO_2. The experimental observations thus tend to confirm the estimates used in the calculations. To revise the calculations to correct for the slight discrepancy between the estimated and experimentally measured values does not seem justified at present since the uncertainties would still remain in the value of ω_2, and they would affect the thermodynamic functions to a greater extent than the uncertainties in ω_1 and ω_3.

Further spectroscopic study of the gaseous molecules CrO_3, MoO_3, and WO_3 over the full spectral range out to 250 cm^{-1} will undoubtedly provide a better insight into the molecular properties, and reduce the uncertainties involved in estimating the molecular configurations and vibrational frequencies of these species.

c. Tungsten Trioxide

Tungsten trioxide, like molybdenum trioxide, was reported to vaporize chiefly as the trimer,[417] which probably has the same structure as the latter, consisting of a 6-membered ring of alternating tungsten and oxygen atoms plus 6 other oxygen atoms doubly bonded to the tungstens. Its one strong infrared absorption band, which is shown in figure 37, could therefore also be assigned to the stretching vibration between oxygen and the rest of the molecule just as in the case of molybdenum trioxide. In fact, the MoO_3 and WO_3 molecules are analogous in most respects; and for the reasons outlined in the preceding paragraph, calculations based on the W_3O_9 spectrum will not be made until further experiments have been conducted.

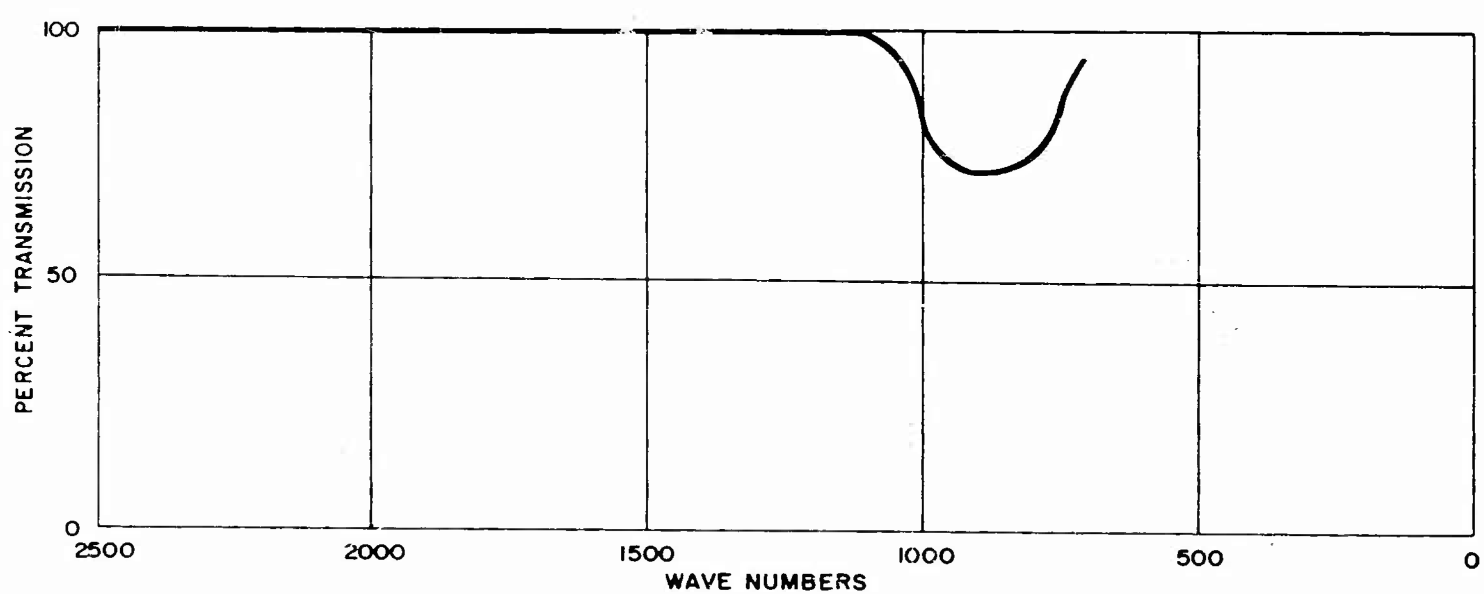

Figure 37 INFRARED ABSORPTION SPECTRUM OF VAPORS FROM TUNGSTEN TRIOXIDE HEATED TO 1640° K

d. Boron Oxides

1) B_2O_3

The infrared absorption spectrum of the vapors from B_2O_3 is shown in figure 38. The path length through the gas for this experiment was approximately 200 feet. Analytical reagent-grade boric anhydride powder was sprinkled on the tungsten ribbon and vaporized at the temperatures given in the figure. From the appearance of the ribbon, there seemed to be no appreciable amount of reaction between the B_2O_3 and the tungsten.

In an article on gaseous B_2O_3 and B_2O_2, White et al[495] have published an infrared emission spectrum of B_2O_3, and from it, have calculated force constants, vibrational frequencies, and thermodynamic functions. The three bands they observed in emission are marked in dotted lines at the bottom of figure 38. The band at 2050 cm^{-1} was the strongest in emission, the one at 1300 cm^{-1} was less strong, and the one at 740 cm^{-1} was the weakest. As figure 38 shows, the relative intensities in absorption are much different from this. Actually, the 2050 cm^{-1} band, White's strongest, does not appear at all in the absorption spectrum, except at the highest temperatures. The effect of the Planck function on the emission intensity would account for only a small part of this intensity discrepancy.

Dows and Porter[496] also studied the infrared emission of B_2O_3 and observed a band in the vicinity of 2000 cm^{-1}. This was the only band they observed. The present results are, therefore, in disagreement with those of two previous groups of investigators on the presence of a strong B_2O_3 band near 2000 cm^{-1}. The absorption spectrum of solid B_2O_3 does not show a band in the vicinity of 2000 cm^{-1}; however, it is similar to (but not identical with) the spectrum presented herein for the vapor. The solid shows bands near 3400 cm^{-1} (O-H?), 1470 cm^{-1}, and 750 cm^{-1}. The spectrum of the solid was recorded from Baker-purified boric anhydride dispersed in a KBr pellet.

An investigation of the vapor of B_2O_3 by the matrix isolation technique has also been reported.[497] The spectrum in this case differs from both of those described above.

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[495] White, D., D. E. Mann, P. N. Walsh, and A. Sommer, J. Chem. Phys. 32, 481 (1960).

[496] Dows, D. A. and R. F. Porter, J. Am. Chem. Soc. 78, 5165 (1956).

[497] Union Carbide Corp., Research in Physical and Chemical Principles Affecting High Temperature Materials for Rocket Nozzles, Semiannual Progress Report to ARPA, Union Carbide Research Inst., Tuxedo, N. Y. and Parma Research Center, Cleveland (31 December 1960).

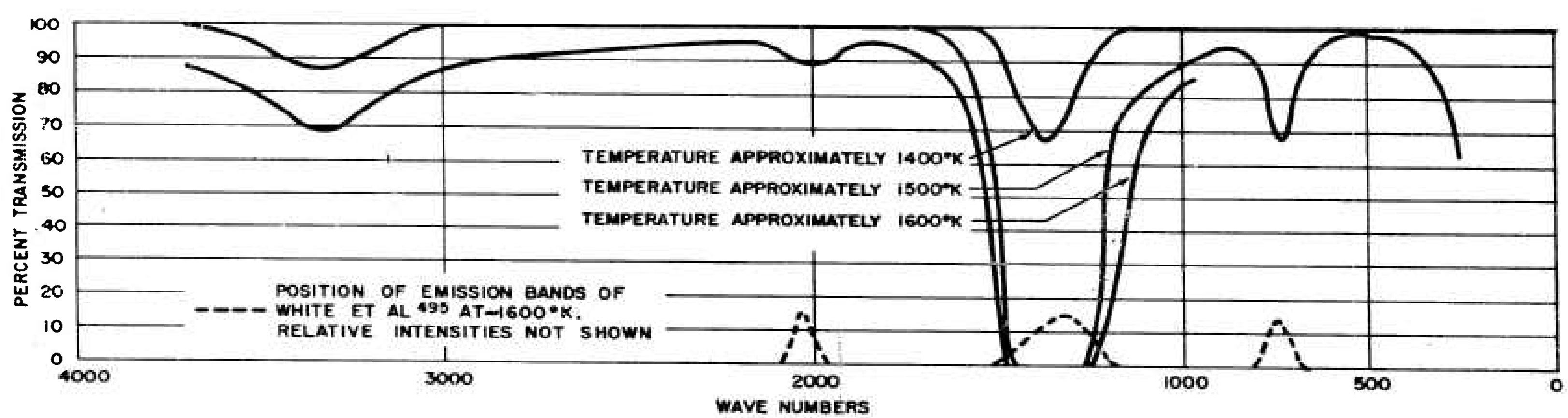

Figure 38 INFRARED ABSORPTION SPECTRUM OF VAPORS FROM BORIC ANHYDRIDE AT TEMPERATURES BETWEEN 1400° AND 1600° K

Because agreement between investigators on the spectrum of B_2O_3 was not achieved, it did not seem justified to make vibrational assignment until the discrepancies had been resolved. If the 1350 cm^{-1} and the 720 cm^{-1} bands in the absorption spectrum in figure 37 come from the same molecule as the 1300 and 740 cm^{-1} emission bands of White et al,[495] then the 2040 cm^{-1} emission band of White et al[495] must have come from some other boron-containing species.

This may also have been the case in the work of Dows and Porter.[496] The investigation of B_2O_3 is being continued at present. Conclusions from the spectrum of B_2O_3 should be held in abeyance until the above discrepancies are removed.

2) B_2O_2

B_2O_2 was prepared both by reaction of MgO with boron and by reaction of B_2O_3 with boron. In each case, a material was produced which gave the infrared absorption spectrum shown by the solid curve in figure 39. The powdered B_2O_3-boron and MgO-boron mixtures were reacted on the tungsten ribbon at a ribbon temperature of approximately 1400°K. The light path through the vapor was approximately 200 feet.

Boron which was isotopically enriched to 90 percent B^{10} was also reacted with MgO and the spectrum of the product recorded. This spectrum is shown by the dotted curve in figure 39. The isotopically enriched elemental boron must have been purer than the naturally occurring isotopic mixture because the 940 cm^{-1} and 1180 cm^{-1} bands are weaker in the B^{10} spectrum. The weakening of these bands plus the fact that they were not isotopically shifted would identify them as impurity bands. The 2550 cm^{-1} band was also not shifted. The 3500 cm^{-1} and 500 cm^{-1} bands were not investigated for isotopic shift. The 3500 cm^{-1} band was most likely due to hydrated species of some kind. Only the 1410 cm^{-1} was isotopically shifted, the shift being between 30 and 50 wave numbers. The latter band was therefore the only one that could be attributed definitely to B_2O_2. If B_2O_2 were a linear, symmetric molecule like its isoelectronic analog, C_2N_2, it should have only one fundamental band in this part of the infrared spectrum.

White et al[495] attributed an emission band at 1890 cm^{-1} to B_2O_2, and from it, calculated thermodynamic functions. However, no absorption was observed at that wavelength in the present work.

The infrared active ω_3 vibration of linear symmetric B_2O_2 should experience an isotopic shift of +42 cm^{-1} in going from B^{11} to B^{10}.

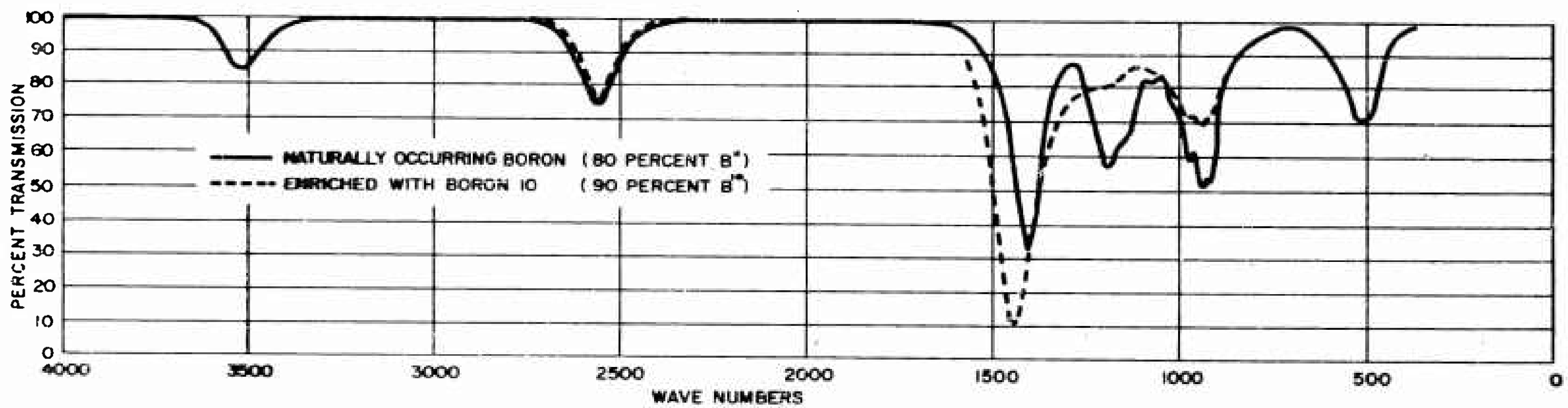

Figure 39 INFRARED ABSORPTION SPECTRUM OF B_2O_2 VAPORS FORMED AT 1400° K

The observed shift of +30 to +50 cm^{-1} thus tends to confirm the chemically plausible assumptions that B_2O_2 is the actual species produced in these reactions and is a linear, symmetric molecule.

The effect of an unknown amount of condensate-particle contamination is an ever-present problem in this type of work. The present apparatus was used in an attempt to minimize the problem, but it remained to be proved that this goal had been achieved. Several experiments were planned at the end of the report period to settle this question. For example, in the case of the B_2O_3 spectrum, it is possible that the 2040 cm^{-1} emission band of White et al[495] comes from B_2O_3 monomer and the 1300 cm^{-1} and 740 cm^{-1} bands come from ploymers or condensate particles.

VI. RECOMMENDATIONS

This report naturally does not bring down the final curtain on the subject of the thermodynamics of highly refractory compounds. A number of important theoretical problems remain to be solved, complete and accurate basic data are still not available for a majority of the species of interest, and many refinements remain to be made in the methods and procedures in current use for estimating missing property data.

The specific heat of condensed phases at high temperatures is a subject worthy of further attention both from the theoretical and experimental standpoints. The theory of vibrational contributions to the specific heat of solids is sufficiently well-advanced, but this suffices only at low temperatures as defined in this project. Some progress has been made in elucidating anharmonicity corrections,[24, 498, 499] but much more needs to be done in applying the theory to specific crystal systems. It appears from what few data are available that other important contributions arise at high temperatures, and that theoretical expressions for their temperature dependence are unavailable.

This lack of theoretical background is felt most in extrapolations of C_p° data to temperatures beyond those of the available data. Such extrapolations should be carried out separately on the various contributions to C_p° from an understanding of how each contribution depends upon the temperature. Such practices as assuming C_p° to be constant or extrapolating empirical equations for its total value introduce large uncertainties which are difficult to estimate since changes in curvature may occur in C_p° versus T at high temperatures (see Fig. 2).

The situation with respect to liquids is the least satisfactory; no attempts have been made to base estimates of C_p° values for liquids on sound theories.

The difficulties of measuring specific heats of condensed phases at high temperatures are very great, and data from various sources most often do not agree. Resorting to experimentation, therefore, does not necessarily result in a reduction in the uncertainties associated with high-temperature thermodynamics. A high degree of confidence in high-temperature thermodynamic property values will come after convincing theoretical interpretations are found for reproducible measurements of C_p° versus temperature.[500]

Samples of interesting high-refractory compounds with a high degree of purity are not readily available, and it is very likely that many of the property determinations in the past have been on samples of doubtful purity unless this has been specifically determined. It would appear that some more work in refining

[498] Ludwig, W., J. Phys. Chem. Solids 4, 283 (1958).

[499] Maradudin, A. A., P. A. Flinn, and R.A. Colderwell-Horsfall, Anharmonic Contributions to Vibrational Thermodynamic Properties of Solids, II. The High Temperature Limit, Sci. Paper 029-G000-P 7 for AFOSR, Westinghouse Research Labs., Pittsburgh (13 February 1961).

[500] Powel, R. Critique on the Analytical Representation of Specific Heat Data, WADC TN 57-308, AD 142 059 (Novembe. 1957).

preparative methods is desirable, so that basic property measurements can be made on pure rather than technical grade samples.

Related to the latter problem is the fact that many interesting refractory compounds can be nonstoichiometric in composition. In fact, theoretical considerations indicate that all compounds can be included in the nonstoichiometric category.[501] Their composition can change whenever some vaporization is allowed to occur at high temperature before it becomes congruent during preparation, study, or end use. Recent studies[501, 502] have shown that this behavior is related to the existence of lattice defects. Nonstoichiometry is an important high-temperature thermodynamic phenomenon which should receive increased attention both from the basic and applied standpoints.

The two types of data most often missing in connection with refractory compounds and their vapor species are heats of formation and spectroscopic constants. Methods for estimating heats of formation have not been developed, and more experimental measurements are needed to fill the gaps in existing data. Although the estimation of spectroscopic constants is often done, eventual confirmation of the values is desirable. In the case of complex polymeric vapor species such as those of the Mo-O and W-O systems, some information about the molecular structure must be available before any estimation of the spectroscopic constants can be attempted. Optical spectroscopic methods appear to be the most neglected of those that can be used in the study of refractory compound vapors.

[501] Anderson, J. S., Significance of Non-stoichiometry on Metal Compounds, In: The Physical Chemistry of Metallic Solutions and Intermetallic Compounds, vol. II, Chemical Publ. Co., N.Y. (1960), p. 234.

[502] Rees, A. L. G., Chemistry of the Defect Solid State, Wiley, N.Y. (1954), 136 p.

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(over)

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3. Carbides
4. Oxides
5. Nitrides
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II. Contract AF 33 (616)-7327
III. Avco Corporation Wilmington, Mass.
IV. S. L. Bender, R. E. Dreikorn, et al
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